# TEXTILE RESEARCH JOURNAL

*Publication of*

TEXTILE RESEARCH INSTITUTE

SEPTEMBER 1961

*One of a series*

# "WHO WANTS A CHEESE FINISH FOR COTTONS?"

These words were elicited on finding some long neglected emulsions behind the Instron in the QC lab. A roquefort grew on one. What grew on the others was even worse.

Speaking of cheese, ***Bacillus brevis*** is a bug with marked morphological similarity to a cheese bacterium named ***Tyrothrix.*** So when a potent antibiotic was isolated from ***B. brevis,*** it wasn't too illogical to call it Tyrothricin. We bring this up because Wallerstein happens to be the prime producer of Tyrothricin. (And here you thought our only products are Rapidase® and Serizyme®!) We make other antibiotics, too, as well as enzymes of medical and pharmaceutical interest. In fact, the name Wallerstein is as meaningful in pharmaceuticals as it is in textiles. But what is the meaning for you? This: the search for new enzymes to be used in pharmaceuticals — and in beer and paper, too, to name a few other of our interests besides textiles — fills our shelves with commercial, development and experimental enzymes of many descriptions. Purity ranges from AR grade on down. Some of these enzymes may be just what an imaginative textile man needs to help out with a particularly knotty problem in research or production.

Interested? Drop us a line detailing your requirements. We may be able to send you one or two enzymes of more than casual interest.

WALLERSTEIN COMPANY
Division of Baxter Laboratories, Inc.
Staten Island 3, N.Y.

Interested in using an enzyme preparation to solubilize alginates? Write Dept. R-9.

# TEXTILE RESEARCH JOURNAL

Volume 31 *September 1961* Number 9



***Editor:***
**Richard K. Toner**

***Production Editor:***
**Dorothy Dana Hollmann**

***Advisory Board***

**Herbert J. Ball**
**Earl E. Berkley**
**John Boulton**
**C. H. Fisher**
**Walter J. Hamburger**
**Milton Harris**
**R. M. Hoffman**
**Harold P. Lundgren**
**Herman Mark**
**George Switlyk**
**Helmut Zahn**



TEXTILE RESEARCH JOURNAL, published monthly at Prince and Lemon Streets, Lancaster, Pa., is devoted to the interest of research in textile and allied industries. It is published by Textile Research Institute.

Manuscripts and communications should be sent to the Publications Department, P.O. Box 625, Princeton, N. J.

Second-class postage paid at Lancaster, Pa.

Subscription rates: $25.00 per year; additional for postage, 50 cents to Canada, $1.00 to all other countries. Single copies, $2.50 each.



Contents copyright © 1961 by Textile Research Institute. Advertising rates supplied on request.


## IN THIS ISSUE


A Study of Reactions between Cotton Cellulose and Difunctional Epoxides. *Ruth R. Benerito, Beverly G. Webre, and J. B. McKelvey* ..... 757

Rate of Felting of Untreated and Shrink-Resistant Wool Fabrics. *J. R. McPhee* ..... 770

The Use of Unheated Air in the Drying of Wool. *J. G. Downes and G. B. McMahon* ..... 779

Moduli of Cotton Fibers and Yarns in Relation to X-Ray Angles. *Louis C. Weiss, Rollin S. Orr, Jerome J. Redmann, and James N. Grant* ..... 787

Kinetic Studies of the Wool–Water System. Part III: The Mechanism of Sorption at High Water Concentrations. *I. C. Watt and J. E. Algie* ..... 793

Wrinkle Resistant Properties of Dialdehyde Cotton. *Charles H. Mack and Wilson A. Reeves* ..... 800

The Spectral Distribution of Sound Produced by Fibers and Fabrics. Part I: Improved Instrumentation. *Walter J. Thorsen and Paul Veneklasen* ..... 804

A New Staining Technique for the Study of Skin and Core of Nylon Yarns. *W. Rhett Berry* ..... 810

The Oxidation of Cotton Cellulose in the Presence of Direct Cotton Dyes. *K. V. Datye, G. M. Nabar, and G. G. Shroff* ..... 813

Radiation-Induced Interaction of Acrylonitrile with Cyanoethylated Cotton. *Robert J. Demint, Jett C. Arthur, Jr., and Wilbur F. McSherry* ..... 821


### LETTERS TO THE EDITOR


The Influence of Surfactants in the Acid Bath on the Loss in Strength of Carbonized Wool. *A. Eleanor Davis, Anna J. Johnson, and Louis R. Mizell* ..... 825

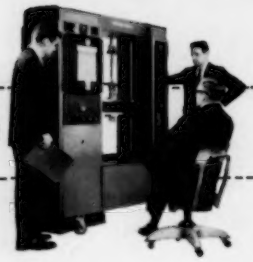
Heat Shrinkage Tensions of Nylon Tire Cord. *W. S. Symes* 827

Twisted Bundle Ballistic Tests of Jute Fiber under Longitudinal Jerk. *S. B. Bandyopadhyay and B. K. Bose* ... 828

IN COMING ISSUES .....inside back cover


REPRINT REQUESTS SHOULD BE DIRECTED TO THE AUTHORS
SEE ARTICLES FOR ADDRESSES

INSTRON



*a new dimension in precision fiber testing*

# Tensile Stress-Strain Properties of Fibers

A new, complete, authoritative 35-page report on the tensile stress-strain properties of eight different fibers, ranging from acetate to wool, is yours for the asking.

Tests, using an Instron, were made on these fibers in air at different temperatures and relative humidities, and in water at different temperatures. In addition, these fibers were studied at various rates of elongation.

Write for Bulletin T-1. It is one of many technical articles covering all fields of testing now ready for you in reprint form.

Discover how Instron's versatility can help you with your problem . . . let us know your field of interest.

INSTRON®

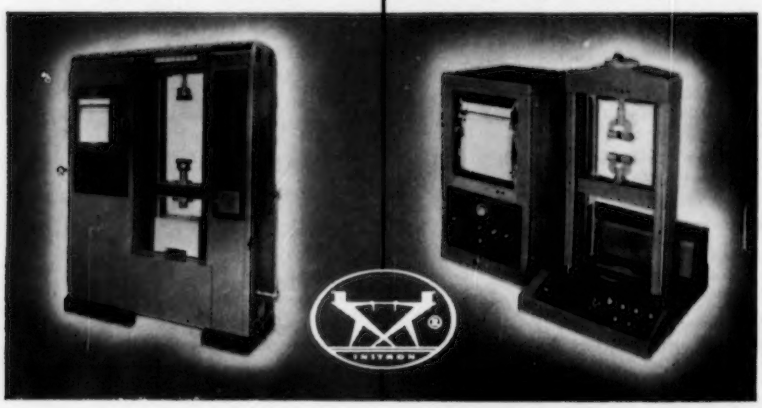
ENGINEERING CORPORATION

2516 WASHINGTON STREET, CANTON, MASS.

EUROPEAN OFFICE: SEEFELDSTRASSE 45, ZURICH, SWITZERLAND

**FLOOR MODEL INSTRON** — *full scale load ranges: 2 grams to 10,000 pounds.*

**TABLE MODEL INSTRON** — *full scale load ranges: 2 grams to 200 pounds.*



SEPTEMBER 1961
VOL. 31 NO. 9

TEXTILE RESEARCH JOURNAL

# A Study of Reactions between Cotton Cellulose and Difunctional Epoxides[1]

**Ruth R. Benerito, Beverly G. Webre, and J. B. McKelvey**

*Southern Regional Research Laboratory,[2] New Orleans, Louisiana*

**Abstract**

Four diepoxides, namely, the diglycidyl ether of 1,4-butanediol, *meso*-butadiene diepoxide, Eponite 100, and vinylcyclohexene dioxide have been applied to cotton print cloth (80 × 80) from methanolic and aqueous solutions in the presence of zinc fluoborate as catalyst. Physical properties imparted to cotton by these diepoxides under various conditions of reaction and cure have been evaluated. Data are presented to show variation of fabric properties with mole ratios of diepoxide: $Zn(BF_4)_2$: AGU (anhydroglucose units of cotton cellulose). It has been found for all except butadiene diepoxide that a given add-on does not result in like fabric properties and that for a certain percentage improvement in dry crease resistance, a higher retention in tensile properties is obtained at the higher AGU: $Zn(BF_4)_2$ mole ratio.

## Introduction

Reactions of epoxy compounds with cotton cellulose have been under investigation in this laboratory for several years. Sodium hydroxide catalyzed reactions and the cellulose–butadiene diepoxide reaction have been subjects of previous reports [9, 10, 8]. A survey of the cellulose–epoxide reaction under conditions of acid catalysis has been reported recently [11]. Four epoxides were found to be most effective in imparting satisfactory wrinkle-resistance properties to cotton. This report is concerned with an evaluation of properties imparted to cotton by diglycidyl ether of 1,4-butanediol, *meso*-butadiene diepoxide, Eponite 100, and vinylcyclohexene dioxide under various conditions of zinc fluoborate catalysis.

## Materials and Methods

*Fabric description.* An 80 × 80 print cloth weighing 3.12 oz./yd.[2] was desized, scoured, and then processed in commercial peroxide bleaching equipment. Experiments were performed on samples approximately 13 in. × 13 in. weighing 10–12 g.

*Chemicals.* Research grade materials kindly furnished by the sources mentioned in Table I[3] were used as such except Araldite RD-2 which was fractionally distilled on occasion to yield its principal component, the diglycidyl ether of 1,4-butanediol (b.p. 125–130° C., 5 mm.).

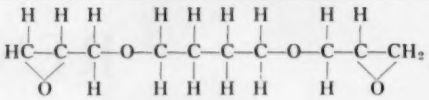
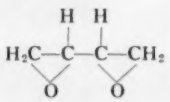
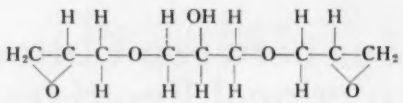
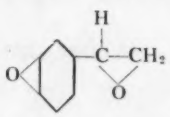
Zinc fluoborate was a 40% aqueous solution of

[1] Presented before the Division of Cellulose Chemistry at the 138th National Meeting of the American Chemical Society in New York, September 11–16, 1960.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[3] Naming a company and/or product by the Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

**TABLE I. Characteristics of Epoxides Used in Investigations**

| Epoxide | Formula of Monomer | Source | Epoxide Equivalent* |
|---|---|---|---|
| Araldite RD-2 |  | Ciba Co. | 0.97 |
| Butadiene diepoxide |  | Union Carbide Corporation | 2.34 |
| Eponite 100 |  | Shell Development Co. | 0.76 |
| Vinylcyclohexene dioxide |  | Union Carbide Corporation | 1.40 |

* Equivalents of acid per 100 g. material as determined by Durbetaki method [4].

technical grade obtained from the Harshaw Chemical Company. Other catalysts were analytical reagent grade chemicals.

*Ultraviolet irradiation.* The source of ultraviolet radiation was a Hanovia Special Lamp (#7400.11) of 500 watts used without filters. Temperatures of irradiated fabrics were measured by means of a calibrated copper-constantan thermocouple.

*Textile testing.* The following textile tests were carried out according to ASTM or Federal Specifications Standard Methods: breaking strengths by the strip method (80 thread count width) on a Scott Tester [1a]; tearing strengths by Elmendorf method [1b]; crease recovery angles by Monsanto method [18] with a 500-g. weight; and moisture regains [1c].

*Microscopical examination.* Methods of optical microscopy were applied to observe the amount of swelling and dissolution of treated fibers in 0.5 *M* cupriethylenediamine (cuene). More detailed information concerning the extent of cross-linking was obtained from electron micrographs by use of specialized techniques on ultrathin (500 Å) cross-sections of treated fibers which had been immersed in 0.5 *M* cuene. These techniques have been described previously [17, 14, 15].

*Density measurements.* Volume densities of fabrics were determined by means of the gradient column technique [12].

## Experimental

*Application of epoxides.* A freshly prepared aqueous or methanolic solution containing desired weight percentages of epoxide and $Zn(BF_4)_2$ was used to twice pad cloth to a 90–100% wet pickup. Samples were cured by two methods: (1) in the oven at 60–175° C. for the desired time, or (2) by irradiation under an ultraviolet light from 5–20 min. After curing was completed, samples were washed in methanol, then distilled water, and were ironed dry and conditioned 24 hr. before weight gains were determined.

## Results and Discussion

In Table I are listed names, sources of supply, formulae of principal monomers, and epoxide equivalents as determined by Durbetaki [4] method.

### *Araldite RD-2–Cellulose Reaction*

*Change in curing conditions.* Exploratory experiments were performed with Araldite RD-2 as received and also with the fractionally distilled diglycidyl ether of 1,4-butanediol. Preliminary experiments showed that like results were obtained with both reagents, and the only advantage of using the monomer was in its complete water solubility.

Data in Table II show effects of curing conditions on weight gain, crease angles, and tensile properties obtained with a freshly prepared methanolic solution

of 11.91% Araldite RD-2 and 1.33% zinc fluoborate. No further improvement in weight gain or crease resistance was obtained by increasing curing temperature above 150° C., as is frequently done in fluoborate catalysis. Curing by irradiation with an ultraviolet light resulted in similar weight gains but higher dry crease angles. For example, a 10-min. irradiation gave a 9% weight gain as did a 5-min. oven cure at 150° C., but the dry angles produced by the former curing method were about 30° higher, as shown in Table II. (A change in crease angles (W + F) of ± 15° is significant.) Both high wet and dry crease angles could be obtained by ultraviolet irradiation, and the ratio of dry to wet angles was greater than unity. Maximum temperatures of cloth as determined by a copper-constantan thermocouple were 84°, 96°, and 99° C. after 5, 10, and 20 min. of irradiation. Experiments performed by curing at temperatures less than 100° C. were required to ascertain if the irradiation of catalyst or lower curing temperature was responsible for improvement of crease recovery. (A source of ultraviolet light accommodated with a cooling jacket was not available.) Curing temperatures between 85–100° C. allowed for higher efficiencies and resulted in excellent wet and dry wrinkle recoveries. A plot of crease recovery angles or add-ons vs. temperature of cure showed two maxima. Typical data for lower temperature cures given in Table II indicate that lower temperatures of cure are accompanied by higher retention of tensile strengths than are obtained with cures at 150° C. A curing temperature of 85° C. resulted in excellent dry crease angles (approximately 280°) accompanied by 70% retention of breaking strength and 50% retention of tearing strength without the use of softeners.

*Change in mole ratios of reactants.* A series of padding solutions in which weight percentages of both Araldite RD-2 and zinc fluoborate catalyst were varied are listed in Table III. Resultant weight gains obtained after curing for 5 min. at 150° C., moisture regains, and crease angles are also given. Crease angles of fabrics treated with these solutions plotted against weight gains expressed as molar ratio of diepoxide to anhydroglucose showed no correlation. This series of solutions was designed to investigate effects of change in mole ratio of epoxide:$Zn(BF_4)_2$:AGU (anhydroglucose units of cotton cellulose) on weight gains and crease resistance properties of resultant fabrics. The AGU:$Zn(BF_4)_2$ mole ratios were 67 for Solutions 1–4; 100 for Solutions 5–8; 200 for Solutions 9 and

**TABLE II. Effects of Method of Cure on Cellulose—Araldite RD-2 Reaction Catalyzed by Zinc Fluoborate***

| Method of curing | Weight gain, % | Breaking strength, % retained | Tearing strength, % retained | Density, g./cm³. | Crease angles† (W + F), deg. | |
|---|---|---|---|---|---|---|
| | | | | | Wet | Dry |
| 5 min., 125° C. oven | 9.4 | | | | 229 | 233 |
| 5 min., 135° C. oven | 8.4 | | | | 237 | 223 |
| 5 min., 150° C. oven | 6.4 | 50.5 | 35.1 | 1.5208 | 245 | 246 |
| 5 min., 150° C. oven | 9.1 | | | | 283 | 262 |
| 5 min., 175° C. oven | 7.1 | | | | 231 | 229 |
| 5 min., UV irradiation‡ | 7.8 | | | | 242 | 248 |
| 10 min., UV irradiation | 5.8 | 68.0 | 41.1 | 1.5220 | 231 | 258 |
| 10 min., UV irradiation | 9.0 | | | | 260 | 290 |
| 20 min., UV irradiation | 6.3 | | | | 232 | 266 |
| 20 min., UV irradiation | 11.3 | | | | 284 | 289 |
| 5 min., 60° C. oven | 3.9 | 86.7 | 59.0 | | 199 | 193 |
| 5 min., 75° C. oven | 6.5 | 77.5 | 50.0 | | 247 | 228 |
| 5 min., 85° C. oven | 10.9 | 72.4 | 47.0 | | 245 | 279 |
| 5 min., 100° C. oven | 13.6 | 64.9 | 37.3 | | 306 | 309 |
| Control | — | (52 lb.) | (1107 g.) | 1.5440 | 166 | 196 |

* All samples of 80² fabric twice padded to 100% wet pickup with freshly prepared methanolic solution containing 11.91% by weight epoxide and 1.33% by weight of $Zn(BF_4)_2$ and cured immediately.

† Average of 3 determinations by Monsanto Crease Angle Method.

‡ Maximum temperatures of cloth were 84°, 92°, and 99° C. after 5, 10, and 20 min. of irradiation.

**TABLE III. Effect of Composition of Padding Solution of Araldite RD-2 on Weight Gains and Crease Angles***

| Solution No. | Composition of pad bath: % Epoxide | Composition of pad bath: % $Zn(BF_4)_2$ | Mole ratio Epoxide:$Zn(BF_4)_2$ | Weight gain, % | Crease angle (W + F), deg.: Wet | Crease angle (W + F), deg.: Dry | Moisture regain, % |
|---|---|---|---|---|---|---|---|
| 1 | 9.05 | 2.03 | 5.26 | 4.2 | 244 | 254 | 5.27 |
| 2 | 11.71 | 1.96 | 7.02 | 6.8 | 259 | 263 | |
| 3 | 16.61 | 1.86 | 10.53 | 8.8 | 276 | 268 | |
| 4 | 28.48 | 1.60 | 21.06 | 15.5 | 280 | 259 | |
| 5 | 6.33 | 1.41 | 5.26 | 2.9 | 203 | 210 | |
| 6 | 11.91 | 1.33 | 10.53 | 7.2 | 240 | 258 | 5.04 |
| 7 | 16.86 | 1.26 | 15.79 | 8.8 | 276 | 268 | |
| 8 | 21.29 | 1.19 | 21.06 | 9.4 | 271 | 268 | |
| 9 | 6.45 | 0.72 | 10.53 | 2.9 | 203 | 210 | |
| 10 | 12.11 | 0.67 | 21.06 | 6.7 | 204 | 212 | 5.16 |
| 11 | 12.22 | 0.34 | 42.12 | 4.2 | — | 167 | 6.14 |
| 12 | 20.67 | 2.31 | 10.53 | 9.4 | 271 | 268 | |
| (control) | — | — | — | — | 166 | 196 | 6.30 |

* 80 × 80 fabric twice padded to 100% wet pickup with freshly prepared methanolic solution of Araldite RD-2 and cured immediately at 150° C. for 5 min.

10; 400 for Solution 11; and 50 for Solution 12. Variations of both wet and dry crease angles (W + F) with mole ratio of epoxide: $Zn(BF_4)_2$ at constant mole ratio of AGU: $Zn(BF_4)_2$ are shown in Figure 1. These data indicate that crease angles imparted depend upon mole ratios of all reactants. For example, in Solutions 3, 6, 9, and 12 of Table III, the mole ratio of epoxide: $ZN(BF_4)_2$ is constant at 10.53, and the crease angle is shown in Figure 1 to increase as the AGU: $Zn(BF_4)_2$ ratio decreases. A given weight percentage add-on in the presence of $ZN(BF_4)_2$ catalyst does not impart like crease angles. For example, Solutions 2, 6, and 10 of Table III were all approximately 12% by weight of epoxide and all resulted in fabrics of approximately 7% weight gain. With Solution 2, in which the AGU: $Zn(BF_4)_2$ ratio was 67, dry and wet crease angles were both about 260°. With Solution 6 in

**TABLE IV. Effects of Method of Cure on Cellulose–Eponite 100 Reaction Catalyzed by Zinc Fluoborate***

| Method of curing | Weight gain, % | Breaking strength, % retained | Tearing strength, % retained | Density, g./cm³. | Crease angles† (W + F), deg.: Wet | Crease angles† (W + F), deg.: Dry |
|---|---|---|---|---|---|---|
| 5 min. 125° C. oven | 7.3 | 58.4 | 40.4 | 1.5225 | 298 | 282 |
| 5 min. 125° C. oven | 9.2 | — | — | — | 252 | 250 |
| 5 min. 135° C. oven | 9.1 | — | — | — | 250 | 231 |
| 5 min. 150° C. oven | 8.9 | — | — | — | 275 | 230 |
| 5 min. 175° C. oven | 10.0 | — | — | — | 293 | 220 |
| 5 min. UV irradiation‡ | 8.8 | — | — | — | 272 | 278 |
| 10 min. UV irradiation | 9.0 | — | — | — | 276 | 272 |
| 10 min. UV irradiation | 6.7 | 67.3 | 44.0 | 1.5314 | 244 | 266 |
| 20 min. UV irradiation | 8.4 | 67.0 | 44.0 | — | 275 | 247 |
| Control | — | (52 lb.) | (1107 g.) | 1.5440 | 166 | 196 |

* All samples of 80² fabric twice padded to 100% wet pickup with freshly prepared methanolic solution containing 11.91% by weight epoxide and 1.33% by weight of zinc fluoborate and cured immediately as indicated.

† Average of 3 determinations by Monsanto Crease Angle Method.

‡ Maximum temperatures of cloth were 84°, 92°, and 99° C. after 5, 10, and 20 min. of irradiation.

which AGU:$Zn(BF_4)_2$ was 100, the dry crease angle was still approximately 260°, but the wet crease angle was reduced to 240°. When the AGU:$Zn(BF_4)_2$ ratio was increased to 200 as in Solution 10, the dry crease angle was reduced by 50°. Further increase of the AGU:$Zn(BF_4)_2$ mole ratio to 400, as in Solution 11, which was still approximately 12% with respect to the epoxide, resulted in a smaller weight gain of only 4% rather than 7% and no increase in either wet or dry crease angles over those of the control fabric. It can also be seen from the data that when the AGU:catalyst ratio was 100 or less, both wet and dry crease angles increased as the epoxide:catalyst mole ratio increased. However, when the AGU:catalyst mole ratio was 200, the crease angles were only approximately 210° for epoxide:catalyst ratios of 10.53 and 21.06 even though the weight gain was 7% at the latter mole ratio. Solution 1 produced wet and dry crease angles of approximately 250° for a weight gain of 4.2%, whereas Solution 11 produced no improvement over the control in either wet or dry crease angles at a like weight gain.

### *Other Epoxide–Cellulose Reactions*

*Change in curing conditions.* Data in Tables IV and V show the effects of curing conditions on weight gain, crease angles, and tensile properties obtained with Eponite 100 and *meso*-butadiene diepoxide when fabric is padded with a methanolic solution of 11.91% epoxide and 1.33% zinc fluoborate.

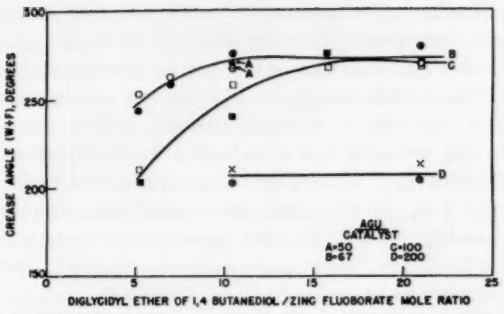



**Fig. 1.** Variation of crease angle with molar ratio of Araldite RD-2:$Zn(BF_4)_2$ at constant AGU:$Zn(BF_4)_2$ mole ratios; triangles, circles, squares, and crosses denote dry angles for A, B, C, and D, respectively; filled in symbols are for corresponding wet angles.

With Eponite 100, optimum crease angles were obtained by use of a 125° C. oven curing temperature, or by a short period of ultraviolet irradiation.

Regardless of method of cure, methanolic solutions of butadiene diepoxide with zinc fluoborate catalysis usually produced less than 2% weight gains. However, even at these small add-ons, excellent wet and dry crease angles and a high degree of cross-linking as indicated by insolubility in cuene were obtained. Because of the volatility of butadiene diepoxide, temperatures above 125° C. were not used. The large increase in dry wrinkle recovery with small increase in weight gain is a most unusual phenomenon. With other cross-linking agents, wet wrinkle recovery usually increases faster than does dry wrinkle recovery at low add-ons.

**TABLE V. Cotton Cellulose–Butadiene Diepoxide Reaction Catalyzed by Zinc Fluoborate***

| Sample | Curing conditions | Weight gain, % dry cotton | DS† | Breaking strength, % retained | Tearing strength, % retained | Density, g./cm³. | Crease angles‡ (W + F), deg. | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | Wet | Dry |
| 1 | 5 min., 125° C. oven | 1.3 | 0.026 | 52.2 | 44.0 | 1.5400 | 247 | 268 |
| 2 | 5 min., 125° C. oven | 0.9 | 0.017 | — | — | — | 235 | 273 |
| 3 | 10 min., 125° C. oven | 2.2 | 0.041 | — | — | — | 254 | 291 |
| 4 | 5 min., UV irradiation** | 0.9 | 0.017 | — | — | — | 225 | 241 |
| 5 | 10 min., UV irradiation | 1.0 | 0.019 | — | — | — | 247 | 243 |
| | 10 min., UV irradiation | 1.0 | 0.019 | 71.7 | — | 1.5410 | 242 | 222 |
| 6 | 15 min., UV irradiation | 1.2 | 0.023 | — | — | — | 234 | 270 |
| 7 | 20 min., UV irradiation | 0.8 | 0.016 | — | — | — | 258 | 232 |
| 8 | 5 min., Autoclaved container 125° C. | 1.5 | 0.028 | — | — | — | 224 | 208 |
| Control | — | — | — | (52 lb.) | (1102 g.) | 1.5440 | 166 | 196 |

* Fabric twice padded to 100% wet pickup with freshly prepared methanolic solution containing 11.91% by weight of epoxide and 1.33% by weight of $Zn(BF_4)_2$.

† Degree of substitution expressed as moles butadiene diepoxide per mole AGU.

‡ Average of 3 determinations by Monsanto Crease Tester (warp + fill).

** Maximum temperatures of cloth were 84°, 92°, 96°, and 99° C. after 5, 10, 15, and 20 min. of irradiation.

Similar experiments with freshly prepared methanolic solutions containing 11.9% vinylcyclohexene dioxide and 1.33% zinc fluoborate always resulted in weight gains varying from 6% to 8% accompanied by a 20% loss in breaking strength, a 50% loss in tearing strength, and a reduction in density to approximately 1.520. Use of ultraviolet irradiations from 5 to 20 min. and oven curing temperatures from 125° to 180° C. over various intervals of time produced wet crease angles of approximately 225° and dry crease angles from 225° to 250°.

*Change in mole ratios of reactants.* All attempts to vary add-ons of butadiene diepoxide on fabric by varying mole ratios of reactants in methanolic padding solutions resulted in 1% to 2% weight gains accompanied by excellent wet and dry crease angles.

Methanolic solutions of vinylcyclohexene dioxide were stable at 25° C. even in the presence of zinc fluoborate, whereas aqueous solutions had to be used within the first two hours because of the fast rate of hydrolysis of the ring oxirane oxygen at 25° C. [2]. Data in Table VI show the effect of composition of methanolic padding solutions of vinylcyclohexene dioxide on weight gains and fabric properties after curing at 150° for 5 min. Again, it is shown that for a given improvement in dry crease resistance, a higher retention of tensile properties is obtained at the higher AGU : catalyst mole ratios. Add-ons as high as 14% resulted in stiff fabrics whose crease angles could not be measured accurately. Variations of wet and dry crease angles with mole ratio of vinylcyclohexene dioxide : $Zn(BF_4)_2$ at constant mole ratio of AGU : $Zn(BF_4)_2$ are shown in Figure 2. As with Araldite RD-2, improvement in both wet and dry crease resistance was obtained at

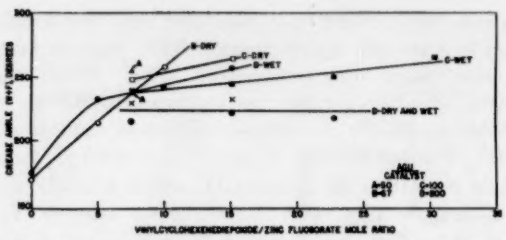



**Fig. 2.** Variation of crease angle with molar ratio of vinylcyclohexene dioxide : $Zn(BF_4)_2$ at constant AGU : $Zn(BF_4)_2$ mole ratios; triangles, circles, squares, and crosses denote dry angles for A, B, C, and D, respectively; filled in symbols are for corresponding wet angles.

**TABLE VI. Effect of Composition of Padding Solutions of Vinylcyclohexene Dioxide on Weight Gains and Fabric Properties***

| Weight % vinyl-cyclohexene dioxide in pad bath | Mole ratios | | Weight gain, % | Crease angles† (W + F), deg. | | Breaking strength, % retained | Tearing strength, % retained | Elong. at break, % | Moisture regains, % |
|---|---|---|---|---|---|---|---|---|---|
| | Epoxide : $Zn(BF_4)_2$ | AGU : $Zn(BF_4)_2$ | | Wet | Dry | | | | |
| 11.5 | 7.60 | 50 | 9.4 | 255 | 238 | 38.9 | 26.7 | 4.7 | 5.68 |
| 16.3 | 11.40 | 50 | 14.7‡ | — | — | — | — | — | — |
| 20.7 | 15.19 | 50 | 21.1‡ | — | — | — | — | — | — |
| 34.3 | 30.38 | 50 | 33.6‡ | — | — | — | — | — | — |
| 9.0 | 5.06 | 67 | 4.3 | 233 | 214 | 48.0 | 34.7 | 6.1 | 5.87 |
| 11.7 | 10.13 | 67 | 9.0 | 242 | 258 | 43.0 | 34.7 | 5.1 | 5.59 |
| 16.6 | 15.19 | 67 | 14.4‡ | 258 | 216 | 47.1 | 20.0 | 4.1 | 5.34 |
| 28.5 | 20.25 | 67 | 20.8‡ | — | — | — | — | — | — |
| 6.3 | 7.60 | 100 | 5.6 | 239 | 249 | 52.0 | 38.0 | 4.7 | 5.94 |
| 11.9 | 15.19 | 100 | 10.2 | 245 | 265 | 58.2 | 40.0 | 4.3 | 5.39 |
| 16.9 | 22.79 | 100 | 14.2‡ | 251 | 224 | 53.3 | 19.3 | 4.1 | 5.45 |
| 21.3 | 30.38 | 100 | 17.0‡ | 266 | 221 | 69.5 | 16.0 | 5.1 | 5.41 |
| 3.3 | 7.60 | 200 | 1.8 | 215 | 230 | 56.2 | 50.0 | 7.0 | 6.28 |
| 6.4 | 15.19 | 200 | 8.6 | 222 | 232 | 66.0 | 47.3 | 6.3 | 5.58 |
| 9.4 | 22.79 | 200 | 7.1 | 217 | 216 | 65.6 | 44.7 | 6.1 | 5.79 |
| 6.5 | 30.38 | 400 | 2.6 | 191 | 213 | 92.5 | 65.3 | 8.3 | 6.60 |
| (control) | — | — | 0.0 | 171 | 176 | | | | 6.32 |

* All samples of 80² fabric twice padded to 100% wet pickup with freshly prepared methanolic solution and cured immediately at 150° C. for 5 min.

† Average of 3 determinations by Monsanto Crease Angle Method.

‡ Samples brittle at this add-on.

epoxide : catalyst mole ratios as low as 5 when the AGU : catalyst ratio was constant at 50 or 67. However, at these low AGU : catalyst ratios, add-ons as high as 14% resulted in stiff fabrics which still had high wet crease angles, but much lowered dry angles. High add-on of this polyepoxide resulted in considerable decreases in tearing strength but had little effect on breaking strength. At add-ons of 20% to 30%, the fabrics were brittle. (Therefore, crease angles at the low AGU : catalyst ratio of 50 could not be plotted in Figure 2.) In contrast, fabric with add-ons of Araldite RD-2 or Eponite 100 as high as 15% still possessed high dry as well as high wet crease resistance, and the angles could be easily determined.

Data in Table VII which illustrate the effect of composition of Eponite 100 padding solutions on fabric properties show that excessively high add-ons of Eponite 100 produce high wet crease resistance. However, the formation of polymer reduces dry crease resistance, causes reduction in tearing strength, and increases breaking strength as compared to samples with lower add-ons obtained at the same AGU : catalyst ratio. For AGU : catalyst mole ratios less than 100, results were similar to those obtained with Araldite RD-2. Excellent wet and dry crease resistance was obtained at epoxide : catalyst ratio as low as 5.26, and no further improvement in wet crease angle was obtained with increase in epoxide : catalyst ratio. However, at high epoxide : catalyst ratios, add-ons as high as 22% resulted in a decrease in dry crease angles. With Eponite 100, high wet and dry crease resistance was obtained at an AGU : catalyst ratio of 200 provided the epoxide : catalyst ratio was increased to 21. In the instance of Araldite RD-2, the latter conditions did not result in wet or dry crease resistance. Variation of both wet and dry crease angles with mole ratio of Eponite 100 : $Zn(BF_4)_2$ at constant mole ratio of AGU : $Zn(BF_4)_2$ are shown in Figure 3. Again, we find that fabric properties depend upon mole ratios of all three reactants and that a given add-on does not result in like fabric properties. Of particular importance are the high retentions of breaking strength (84%), tearing strength (80%), and moisture regain (6%) for high dry (265°) and high wet (255°) crease resistance at the AGU : $Zn(BF_4)_2$ mole ratio of 200. Com-

**TABLE VII. Effect of Composition of Padding Solutions of Eponite 100/$Zn(BF_4)_2$ on Weight Gains and Fabric Properties***

| Eponite 100 in pad bath, weight % | Mole ratios | | Weight gain, % | Crease angles† (W + F), deg. | | Breaking strength, % retained | Tearing strength, % retained | Moisture regain, % |
|---|---|---|---|---|---|---|---|---|
| | Eponite 100 : $Zn(BF_4)_2$ | AGU : $Zn(BF_4)_2$ | | Wet | Dry | | | |
| 11.5 | 5.26 | 50 | 12.0 | 275 | 260 | 60.9 | 28.0 | 4.98 |
| 20.7 | 10.53 | 50 | 22.3‡ | 267 | 239 | 59.5 | 20.0 | 5.61 |
| 34.3 | 21.06 | 50 | 35.3‡ | 289 | 240 | 84.1 | 17.3 | 5.59 |
| 9.0 | 5.26 | 67 | 5.6 | 264 | 266 | 51.9 | — | — |
| 11.7 | 7.02 | 67 | 7.9 | 274 | 282 | 50.5 | — | — |
| 16.6 | 10.53 | 67 | 12.2 | 272 | 274 | 57.7 | — | — |
| 28.5 | 21.06 | 67 | 22.2‡ | 283 | 230 | 72.1 | — | — |
| 28.5 | 21.06 | 67 | 33.7‡ | 263 | 230 | 73.0 | 13.3 | 5.45 |
| 6.3 | 5.26 | 100 | 7.5 | 257 | 282 | 67.1 | 49.3 | 5.64 |
| 11.9 | 10.53 | 100 | 9.1 | 252 | 282 | — | — | — |
| 16.9 | 15.79 | 100 | 13.7 | 264 | 272 | 74.3 | 43.3 | 5.67 |
| 21.3 | 21.06 | 100 | 15.4 | 266 | 277 | 75.5 | 42.0 | 5.17 |
| 3.3 | 5.26 | 200 | 3.1 | 196 | 216 | 65.4 | 67.3 | 6.29 |
| 6.5 | 10.53 | 200 | 4.7 | 222 | 246 | 74.4 | 74.7 | 6.13 |
| 12.1 | 21.06 | 200 | 8.8 | 256 | 266 | 83.5 | 78.7 | 6.03 |
| Control | 0 | 0 | 0 | 177 | 171 | (50.9 lb.) | (1000 g.) | 6.32 |

* All samples of 80² fabric twice padded to 100% wet pickup with freshly prepared methanolic solution and cured immediately at 125° C. for 5 min.

† Average of 3 determinations by Monsanto Crease Angle Method.

‡ Tendency of fabric to curl at high add-on makes angles unreliable.

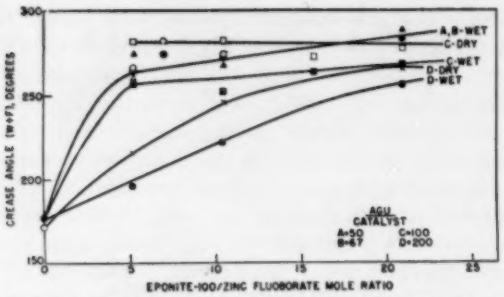



**Fig. 3.** Variation of crease angle with molar ratio of Eponite 100 : $Zn(BF_4)_2$ at constant AGU : $Zn(BF_4)_2$ mole ratios; triangles, circles, squares, and crosses denote dry angles for A, B, C, and D, respectively; filled in symbols are for corresponding wet angles.

parable high wet and dry angles obtained at an AGU : catalyst ratio of 100 were accompanied by 75% retention of breaking strength but only 43% retention of tearing strength and a 5.5% moisture regain. Decrease of the AGU : catalyst ratio to 50 resulted in 70% breaking strength retention and only 28% tearing strength retention and 5.0% moisture regain for comparable wet and dry crease angles.

Figures 4, 5, and 6 show the variation of moisture regain with crease angle for cottons finished with Araldite RD-2, vinylcyclohexene dioxide, and Eponite 100, respectively, with zinc fluoborate catalysis. Although there is some regular decrease in moisture regain with increase in dry crease angle for cottons finished with all three diepoxides, the variation is not always a smooth curve as observed with some less hydrophilic finishing agents such as DMEU [13]. Fluoborate catalyzed butadiene diepoxide finished fabrics possessing at least 100° improvement in dry crease angles had moisture regains of only 0.2–0.3% less than untreated fabrics.

For a given improvement in dry crease resistance, fabrics treated with Eponite 100 or vinylcyclohexene dioxide possessed a higher moisture regain than fabric finished with Araldite RD-2. High moisture-regain values are indicative of hydrophilic finishing agents. With diepoxides, at least one hydroxyl group is formed for every cellulosic hydroxyl reacted. These hydroxyl groups should be of value in contributing to the comfort factor of crease resistant fabrics.

*Catalysis by zinc fluoborate in aqueous solution.* Addition of diepoxide from aqueous solution catalyzed by zinc fluoborate and improvement in both wet and dry wrinkle recovery were obtained with diglycidyl ether of 1,4-butanediol, Eponite 100, and vinylcyclohexene dioxide. Typical data obtained with approximately 18% diepoxide and 2% zinc fluoborate applied by the pad, dry, cure method are given in Table VIII. Usually, treatment at this temperature (140°) is 60–70% efficient and is accompanied by usual losses of 50–60% of tearing strength and 30–40% of the breaking strength for dry crease angles as high as 280°.

Rates of hydrolysis of various diepoxides in acidic

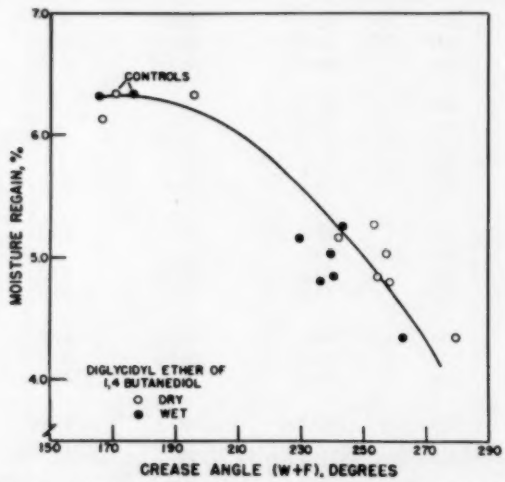



**Fig. 4.** Variation of moisture regain with crease angle for cotton treated with Araldite RD-2.

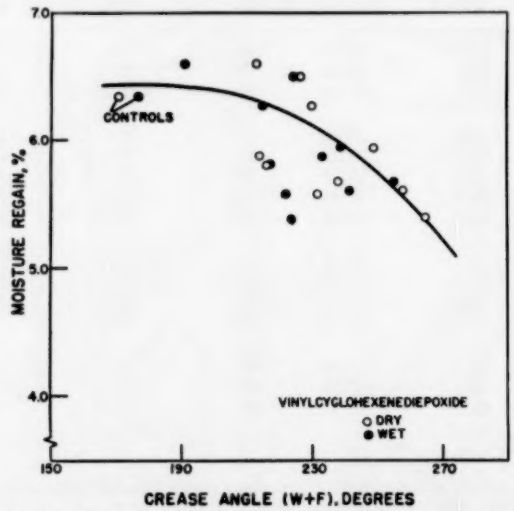



**Fig. 5.** Variation of moisture regain with crease angle for cotton treated with vinylcyclohexene dioxide.

**TABLE VIII. Properties of Fabrics Treated with Aqueous Solutions of Diepoxides***

| Epoxide | Epoxide equivalent | Padding solution, % epoxide | Weight gain, % | Crease angles (W + F), deg. | | Breaking strength, % retained | Tearing strength, % retained |
|---|---|---|---|---|---|---|---|
| | | | | Wet | Dry | | |
| Araldite RD-2 | 0.97 | 18.5 | 13.0 | 244 | 265 | 65.6 | 40.9 |
| Eponite 100 | 0.76 | 18.5 | 12.6 | 274 | 284 | 62.7 | 38.6 |
| Vinylcyclohexene dioxide | 1.40 | 17.0 | 9.7 | 245 | 267 | 69.1 | 39.7 |

* All fabrics were 80 × 80 print cloth twice padded to 100% wet pickup with aqueous solution of diepoxide containing 2% zinc fluoborate and cured at 140° C. for 3 min.

media are under investigation in this laboratory [2]. For a few diepoxides, the rapid increase in rate of hydrolysis with increase of temperature even in the absence of added catalyst can account for the lack of addition of diepoxide to cellulose in many instances. The rapid increase of specific reaction rate constants with rise in temperature indicates that curing temperatures lower than those recommended earlier [16] for epoxide resin cures catalyzed by fluoborate would increase the efficiency of cellulose–diepoxide reactions. The fact that fluoborates yield boron trifluoride at temperatures as low as 75° C. [5, 6] makes it unnecessary to use extremely high curing temperatures to initiate catalysis with zinc fluoborate. These ideas are substantiated by the increase in efficiency of the Araldite RD-2–cellulose reaction when curing temperatures are lowered to between 85–100° (Table II). There is also a greater loss in breaking strength and tearing strength for a given dry crease resistance as the temperature of cure is increased to 150° or above. For example, a 6.0% weight gain of Araldite RD-2 obtained by curing samples at 100°, 125°, and 150° C. resulted in wet and dry crease angles of approximately 240°. The percentage of breaking strength retained decreased from 68% to 63% to 56%, and the tearing strength retention decreased from 52% to 49% to 38% as the curing temperatures increased from 100° to 125° to 150° C.

Data in Table IX show that there is a decrease in breaking and tearing strengths as the temperature of cure is increased from 100° to 150° C. when the padding solution is an aqueous solution of 9.9% Araldite RD-2 and 1.1% $Zn(BF_4)_2$. It is interesting to note that for a given weight gain and comparable crease resistant properties, both aqueous solutions and methanolic solutions (Table II) of Araldite RD-2 produced similar reductions in tearing and breaking strengths at a given curing temperature. Drying of fabrics at a lower temperature before curing at 100° or 150° C. resulted in identical weight gains but some improvement in dry crease resistance and tearing strength. In aqueous solutions, the reaction is approximately 60% efficient, and with proper curing methods, at least 55% of the tearing strength and approximately 70% of the breaking strength can be retained when wet and dry crease angles of 250° are imparted. Data in Table IX, when compared to those in Table VIII, show that it is not necessary to use padding solutions of approximately 20% solid content as is usually recommended in order to obtain high dry crease resistance [19].

Table X contains similar data obtained with 9.7% aqueous solution of vinylcyclohexene dioxide and 1.1% zinc fluoborate. With this diepoxide, the more concentrated solution (Table VIII) imparted the better crease resistance. Solutions of approximately 10% resulted in lower weight gains, maximum dry crease angles of 240°, but very little improvement in wet crease resistance. Recently, Galligan et al. [7] have reported use of 17% aqueous solutions of vinyl-

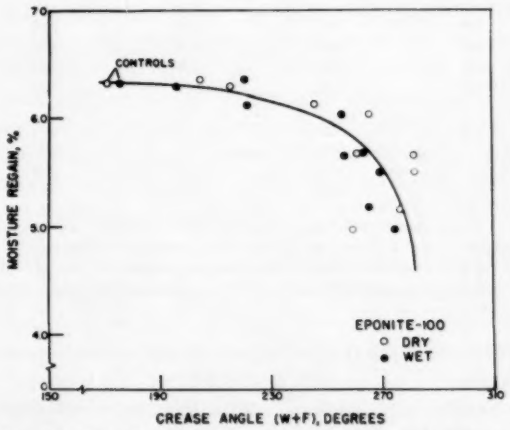



Fig. 6. Variation of moisture regain with crease angle for cotton treated with Eponite 100.

**TABLE IX. Effects of Method of Cure on Cellulose–Araldite RD-2 Reaction Catalyzed by Zinc Fluoborate in Aqueous Solutions***

| Method of cure | | Weight gain, % | Crease angles (W + F), deg.† | | Breaking strength, % retained | Tearing strength, % retained | Moisture regain, % |
|---|---|---|---|---|---|---|---|
| Minutes | Degrees C. | | Wet | Dry | | | |
| 5 | 100 | 5.9 | 223 | 227 | 68.3 | 52.4 | — |
| 5 | 125 | 5.9 | 239 | 238 | 63.0 | 48.8 | — |
| 5 | 150 | 6.1 | 242 | 248 | 56.5 | 37.9 | — |
| 5 | 40 | — | 150 | 170 | — | — | 6.10 |
| 20<br>7 | 40<br>60 | 1.1 | 166 | 181 | 96.0 | 96.0 | 6.23 |
| 20<br>7 | 40<br>75 | 3.4 | 188 | 202 | 74.1 | 66.0 | 5.81 |
| 20<br>7 | 40<br>85 | 4.4 | 213 | 248 | 72.8 | 59.3 | 5.35 |
| 20<br>7 | 40<br>100 | 5.8 | 237 | 259 | 66.7 | 53.3 | 4.82 |
| 20<br>7 | 40<br>150 | 6.3 | 263 | 280 | 55.1 | 43.3 | 4.34 |
| 7 | 60 | 0.6 | 162 | 182 | 100.0 | 100.0 | 6.54 |
| 7 | 75 | 2.7 | 203 | 201 | 82.8 | 76.7 | 6.36 |
| 7 | 85 | 4.3 | 215 | 223 | 79.6 | 61.3 | 5.48 |
| 7 | 100 | 5.3 | 230 | 243 | 68.1 | 58.0 | 5.17 |
| 7 | 150 | 6.2 | 241 | 255 | 54.6 | 41.3 | 4.85 |
| Control | | — | 177 | 171 | (50.9 lb.) | (1000 g.) | 6.32 |

* Samples of 80² fabric twice padded to 100% wet pickup with freshly prepared aqueous solutions containing 9.72% diepoxide and 1.1% zinc fluoborate and cured as indicated.

† Average of 3 determinations by Monsanto Crease Angle Method.

**TABLE X. Effects of Method of Cure on Cellulose–Vinylcyclohexene Dioxide Reaction Catalyzed by Zinc Fluoborate in Aqueous Solutions***

| Drying temperature, deg. C. | Temperature of cure,† deg. C. | Weight gain, % | Crease angles‡ (W + F), deg. | | Breaking strength, % retained | Elongation at break, % | Tearing strength, % retained |
|---|---|---|---|---|---|---|---|
| | | | Wet | Dry | | | |
| 40 | 85 | 3.6 | 210 | 219 | 82.3 | 7.5 | 72.0 |
| 40 | 100 | 4.3 | 216 | 238 | 76.8 | 6.7 | 64.0 |
| 40 | 125 | 5.6 | 207 | 233 | 74.3 | 6.5 | 55.3 |
| 40 | 150 | 6.1 | 209 | 240 | 69.1 | 6.7 | 48.0 |
| — | 85 | 4.2 | 194 | 197 | 86.8 | 7.9 | 80.0 |
| — | 100 | 4.7 | 205 | 208 | 80.9 | 7.2 | 76.0 |
| — | 125 | 4.9 | 208 | 213 | 78.6 | 7.0 | 62.7 |
| — | 150 | 5.3 | 195 | 226 | 71.3 | 6.5 | 54.7 |

* Samples of 80² fabric twice padded to 100% wet pickup with freshly prepared aqueous solutions containing 9.72% diepoxide and 1.1% zinc fluoborate and cured as indicated.

† All cured for 7 min.; only first four dried 20 min. at 40° C. before curing.

‡ Averages of 3 determinations by Monsanto Crease Angle Method.

cyclohexene dioxide to impart excellent wash–wear finishes.

Similar data obtained with a solution which contained 10.6% Eponite 100 and 1.19% zinc fluoborate are recorded in Table XI. Since Eponite 100 was not completely soluble in water and the monomer was not easily fractionated, an aqueous solution containing 33.5% methanol was used. Excellent wet and dry crease resistance accompanied by approximately 55% retention of tearing strength and 65%

**TABLE XI. Effects of Method of Cure on Cellulose–Eponite 100 Reaction Catalyzed by Zinc Fluoborate in Aqueous Solutions***

| Drying temperature, deg. C. | Temperature of cure,† deg. C. | Weight gain, % | Crease angles‡ (W + F), deg. | | Breaking strength, % retained | Elongation at break, % | Tearing strength, % retained |
|---|---|---|---|---|---|---|---|
| | | | Wet | Dry | | | |
| 40 | 85 | 7.3 | 225 | 233 | 67.6 | 6.5 | 60.7 |
| 40 | 100 | 8.0 | 243 | 257 | 68.8 | 6.6 | 59.3 |
| 40 | 125 | 8.3 | 254 | 265 | 61.2 | 5.5 | 53.3 |
| 40 | 150 | 8.3 | 247 | 258 | 48.7 | 4.6 | 40.7 |
| — | 85 | 6.7 | 215 | 219 | 72.8 | 6.5 | 66.0 |
| — | 100 | 5.9 | 229 | 221 | 73.5 | 7.4 | 65.3 |
| — | 125 | 8.5 | 239 | 246 | 63.4 | 5.7 | 49.3 |
| — | 150 | 10.0 | 246 | 248 | 52.5 | 5.8 | 42.0 |

* Samples of 80² fabric twice padded to 100% wet pickup with freshly prepared aqueous solutions containing 10.6 weight % Eponite 100, 1.19% zinc fluoborate, and 33.5% methanol.
† All cured 7 min.; only first four dried 20 min. at 40° C. before curing.
‡ Average of 3 determinations by Monsanto Crease Angle Method.

retention of breaking strength were obtained at a 75% efficiency.

*Microscopical examinations.* Information concerning uniformity of reaction or extent of cross-linking of cellulose by various epoxides can be obtained by studies of optical micrographs and electron micrographs. Both pictures are obtained by modifications of the method of swelling cotton cellulose in cupriethylenediamine (cuene) [17, 14, 15]. First, the behavior of treated fibers immersed in 0.5 *M* cuene for 30 min. are observed with the light microscope at 250 × magnification. If there is only swelling or slight solubility, an ultrathin cross-section of the fiber (500 Å) after immersion in 0.5 *M* cuene for 30 min. is examined by means of the electron microscope at 5250 × magnification.

If there is little or no reaction between cotton fibers and epoxides, the whole fiber dissolves in 0.5 *M* cuene. An ultrathin cross-section of untreated native cotton cellulose fibers completely disperses when immersed in 0.5 *M* cuene, and only fragments of noncellulosic material remain [15]. Polymer impregnation without actual combination of monomer or polymer with the cellulose molecule gives a different electron micrograph in that the cellulosic material is removed, but the polymer remains intact. In those instances where the epoxide has reacted with cellulosic fiber, the cellulosic material is not dispersed in cuene, but swelling occurs depending on the frequency of cross-links formed by the epoxides. A small amount of cross-linking leads to greater swelling; with extensive cross-linking there is less swelling or more restriction in cross-sectional enlargement.

Table XII is a summary of microscopic observations made after cuene immersion of fibers and ultrathin cross-sections of fibers removed from fabrics treated with the various epoxides. With butadiene diepoxide and the diglycidyl ether of 1,4-butanediol, evidence of cross-linking was excellent. Cellulose was so uniformly cross-linked that the electron micrographs on ultrathin cross-sections after im-

**TABLE XII. Degree of Cross-linking of Cotton by Diepoxides as Indicated by Microscopical Examination of Products after Immersion in Cupriethylenediamine***

| Treatment with $Zn(BF_4)_2$ catalyst | Cure | |
|---|---|---|
| | Oven | UV |
| Butadiene diepoxide | | |
| fiber | High | Medium (S) |
| cross-section | High | Medium |
| Diglycidyl ether of 1,4-butanediol | | |
| fiber | High | High (S) |
| cross-section | High | High (S) |
| Eponite 100 | | |
| fiber | High | Medium (S) |
| cross-section | High | Medium (S) |
| Vinylcyclohexene dioxide | | |
| fiber | Low | Medium (S, d) |
| cross-section | None | Medium (S) |

* (High) indicates no dissolution after immersion in 0.5 *M* cupriethylenediamine for 30 min.; an (S) indicates some enlargement or swelling but no dissolution; (d) indicates some dissolution, but fiber or ultrathin cross-section still intact; (High), (Medium), (Low), and (None) indicate comparative degrees of cross-linking.

mersion in 0.5 *M* cuene were exactly like those of native cellulose which had not been placed in cuene. There was no swelling or enlargement of cross-sectional areas. There was evidence of a high degree of cross-linking by Eponite 100. The level of cross-linking obtained with vinylcyclohexene dioxide catalyzed by zinc fluoborate was much lower than that obtained with the other three diepoxides.

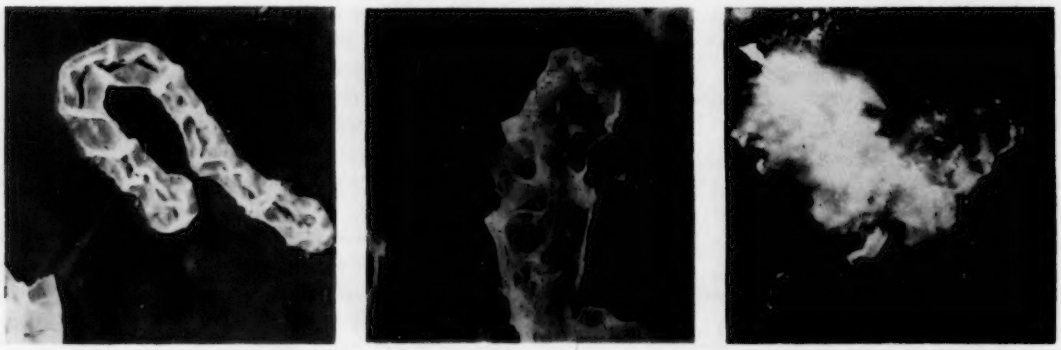
The electron micrographs in Figure 7 are illustrative of ultrathin cross-sections of treated fibers after 30 min. immersion in 0.5 *M* cuene. Micrographs a, b, and c are typical of high, medium, and low degrees of cross-linking, respectively. Fabric respresented in 7a had an 8.5% weight gain of the diglycidyl ether of 1,4-butanediol and wet and dry crease angles of 231° and 258°, respectively. Micrograph 7b was that of a fabric with a 7.3% weight gain of Eponite 100 possessing crease angles of 298° wet and 289° dry. The fabric pictured in 7c had a weight gain of 7.4% vinylcyclohexene dioxide and wet and dry angles of 233° and 253°, respectively.

*Effect of Softeners as Aftertreatment*

Previous work [3] has shown that the dry crease resistance imparted by certain cross-linking agents can be improved by use of a softener applied as an aftertreatment. Preliminary experiments have shown that the usual increase in dry crease resistance is observed after application of softener in the instances of Eponite 100, Araldite RD-2, and vinylcyclohexene dioxide treated cotton, but that dry crease resistance was lowered in the instance of butadiene diepoxide. Data in Table XIII are typical of differences in fabric properties observed after the application of a 1% solution of Primenit VS (octadecylethyleneurea) as a softener.

## Summary

With the proper technique of application, diepoxides can be used for the production of durable crease resistance finishes for cotton fabrics. All four diepoxides studied in this investigation can be successfully applied from methanolic solutions in the presence of zinc fluoborate catalyst. Only the butadiene diepoxide fails to impart crease resistance when applied from aqueous solutions. It is also the only one of the diepoxides whose addition to cellulose could not be controlled by variation of curing conditions or changes in diepoxide : $Zn(BF_4)_2$ : AGU mole ratios. With the proper selection of mole ratios for the other three diepoxides, it is possible to achieve excellent wet and dry crease resistance at relatively low add-ons without excessive loss of tensile properties. For a given mole ratio of reactants, a lower curing temperature (85–125°) gives better tensile properties for a given improvement in crease recovery than does a higher curing temperature (150–180°). Data indicate that a relatively low add-on of diepoxide is required to impart the desired degree of crease resistance. At a given AGU : catalyst mole ratio, further addition of diepoxide, probably resulting from *in situ* self polymerization, reduces dry crease resistance and tearing strength but has little effect on wet crease resistance or breaking strength. Excessive add-ons finally result in stiff or brittle fabrics.



(a) (b) (c)

**Fig. 7.** Electron micrographs of ultrathin cross-sections of diepoxide treated fibers after 30 min. immersion in 0.5 *M* cupriethylenediamine (platinum shadowing, 5250×): (a) diglycidyl ether of 1,4-butanediol (high); (b) Eponite 100 (medium); and (c) vinylcyclohexene dioxide (low).

**TABLE XIII. Effect of a Primenit VS Aftertreatment on Properties of Fabric Treated with Epoxides**

| Epoxide | Add-on, % | | Breaking strength, % retained | | Tearing strength, % retained | | Monsanto wrinkle recovery (W + F), deg. | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | T | | T + A | |
| | T* | T + A† | T | T + A | T | T + A | Wet | Dry | Wet | Dry |
| Control | 0 | | 100 | | 100 | | 166 | 196 | | |
| Eponite 100 | 7.3 | 8.2 | 58.4 | 58.1 | 40.4 | 48.6 | 298 | 282 | 283 | 305 |
| Araldite RD-2 | 6.4 | 7.3 | 50.5 | 50.5 | 35.1 | 40.8 | 245 | 246 | 297 | 279 |
| Butadiene diepoxide | 1.3 | 1.0 | 52.2 | 47.6 | 44.0 | 46.8 | 247 | 268 | 228 | 259 |
| Vinylcyclohexene dioxide | 5.2 | 7.4 | 78.7 | 64.5 | — | 46.8 | 227 | 227 | 268 | 249 |

* All fabrics were 80 × 80 print cloth twice padded to 100% pickup with freshly prepared methanolic solutions containing 11.91% by weight of the epoxide and 1.33% by weight of $Zn(BF_4)_2$, immediately cured for 5 min. at 125° C. (Araldite at 150° C.), washed in methanol, and ironed dry.

† Aftertreatment consisted of padding samples through a 1% solution of octadecylethyleneurea using 2 dips and 2 nips with a maximum squeeze roll pressure, oven drying at 85° C. for 30 min., and then rinsing with hot tap water.

Both wet and dry wrinkle recovery angles were found to be inversely related to moisture regain values of the finished fabrics. While densities of finished fabrics were lower than that of the control, little correlation was found between dry crease angles and densities.

## Acknowledgments

The authors wish to express their appreciation to Mr. Verne W. Tripp and Miss Anna T. Moore for preparation and interpretation of optical and electron micrographs, to Mr. George Pittman for preparation of graphs, to Miss Betsy Banta and to members of the Textile Testing Investigations for physical testings.

## Literature Cited

1. American Society for Testing Materials, ASTM Designations: (a) D39–59; (b) D1424–59, (c) D629–56, Philadelphia, Pa.
2. Berni, R. J., Webre, Beverly G., Benerito, Ruth R., and McKelvey, J. B., in process.
3. Drake, G. L., Jr. and Guthrie, J. D., TEXTILE RESEARCH JOURNAL **29**, 155–164 (1959).
4. Durbetaki, A. J., *Anal. Chem.* **28**, 2000–2001 (1956).
5. Funk, H. and Binder, F., *Z. anorg. u. allgem. Chem.* **155**, 327–332 (1926).
6. Funk, H. and Binder, F., *Z. anorg. u. allgem. Chem.* **159**, 121–124 (1926).
7. Galligan, John, Sookne, A. M., Adams, J. T., Jr., Guest, Howard, and Lourigan, G. H., TEXTILE RESEARCH JOURNAL **30**, 208–222 (1960).
8. Klein, Elias, McKelvey, J. B., and Webre, Beverly G., *J. Phys. Chem.* **62**, 286–288 (1958).
9. McKelvey, J. B., Webre, Beverly G., and Klein, Elias, TEXTILE RESEARCH JOURNAL **29**, 918–925 (1959).
10. McKelvey, J. B., Benerito, Ruth R., Webre, Beverly G., and Berni, R. J., presented at 3rd Cellulose Conference, Syracuse, New York, October 26–28, 1960.
11. McKelvey, J. B., Webre, Beverly G., and Benerito, Ruth R., *Am. Dyestuff Reptr.* **49**, 804–809 (1960).
12. Orr, R. S., Weiss, L. C., Moore, H. B., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 592–600 (1955).
13. Perkerson, F. S., Reeves, W. A., and Tripp, V. W., TEXTILE RESEARCH JOURNAL **30**, 944–954 (1960).
14. Rollins, Mary L., Moore, Anna T., and Tripp, V. W., *Proc. Intern. Conf. Electron Microscopy* **4**, 712–715 (1960).
15. Rollins, Mary L., deGruy, Ines V., Tripp, V. W., and Moore, Anna T., *Am. Soc. Testing Materials, Spec. Tech. Publ.* No. *257*, 153–165 (1959).
16. Schroeder, C. W. and Condo, F. E., TEXTILE RESEARCH JOURNAL **27**, 135–145 (1957).
17. Tripp, V. W., Reeves, W. A., and Perkerson, F. S., presented before the Division of Polymer Science of the American Chemical Society at Atlantic City, N. J., September 1959.
18. U. S. Federal Supply Service, Federal Specification CCC–T–191b, Method 5212, Washington, D. C., U. S. Govt. Print. Off. (1951).
19. Williams, C. R., *Am. Dyestuff Reptr.* **49**, P431–P438 (1960).

*Manuscript received January 6, 1961.*

# Rate of Felting of Untreated and Shrink-Resistant Wool Fabrics

**J. R. McPhee**

*Division of Textile Industry, Wool Research Laboratories, Commonwealth Scientific and Industrial Research Organization, Geelong, Australia*

## Abstract

Shrinkage–time curves for a range of wool fabrics, and the effect of various shrink-proofing treatments on these curves, have been studied. Felting rates of untreated fabrics depend on fabric structure and applied force in the way previously established [e.g., 3, 13, 15]. The shrinkage–time curves of treated fabrics show two definite stages, an initial portion indicating a very low felting rate, followed by a second stage where felting may be much more rapid. For a given fabric structure and given applied force, the felting rates of both stages, and the times at which the second stage begins, depend on the degree of treatment. The two-stage curves indicate two distinct steps in the felting of the fabrics and are not due to the fibers being unevenly treated.

Frictional properties of treated Merino 64's fibers show no correlation with shrink resistance, and the results are qualitatively different from those found with Lincoln 36's.

The importance of defining washing conditions when testing shrink-resistant wool fabrics is again emphasized by results showing that quite different impressions can be gained by washing in different machines and thereby applying different mechanical forces to the fabrics. In an extreme case, a treated fabric of loose structure, when washed for a given time in two different machines, can appear to be either completely shrinkproofed or scarcely shrink-resistant at all.

## Introduction

Assemblies of wool fibers felt when agitated in aqueous solutions. Felting is, very simply, due to rootward fiber movements and fiber entanglements resulting from undirected applied mechanical forces [30]. The rate of felting, under given conditions, varies with fiber type [42, 46, 48, 49] and the structure of the fiber assembly [3, 5, 13, 15, 17, 20, 52]. External conditions influencing the rate of felting are mechanical action [8, 41, 52], the felting medium [4, 8, 49, 53, 54] and the temperature [8, 18, 32, 39, 40, 41, 47, 49], and the rate of felting decreases with time [8, 10, 20, 52].

Rate of felting is decreased by increasing the twist in a yarn [e.g., 3, 52]. The rate of felting of fabrics depends on the tightness of the weave, which can be expressed as a compactness ratio [3], or of the knit, which can be expressed as the stitch length [37], and also on the applied force [52]. Once the applied force is greater than the minimum necessary to cause felting, the felting rate is increased as the applied force is increased over a large range until, above a certain relatively high force, the rate becomes approximately constant [52].

This paper describes the results of felting shrinkage tests on untreated fabrics and on fabrics treated for shrink resistance by the common industrial processes. The tests were carried out by applying different forces in a variety of washing machines having different mechanical actions.

## Experimental

### *Materials*

All fabrics used were made from Merino 64's wool. Fabric structures are given in Table I. The woven fabrics used all felted at about the same rate in both warp and weft directions.

Fiber properties were measured on single fibers withdrawn from samples of Fabric 1, either untreated or after treatments as specified.

### *Methods*

*Measurement of felting shrinkage.* Fabric samples, 12 in. square, were allowed to relax in 0.05% soap

(sodium stearate) solution (pH about 9) at 45° for 30 min. and their areas measured. They were then washed in 0.05% soap solution at 45° for given times and re-measured, the required load in the machines being given by 12-in. squares of cotton fabric.

Five common home washing machines were used having three distinct mechanical actions:

Machine A—"Agitator type." Washing action was given by three centrally mounted reversing vanes moving at 68 cycles/min. The bowl dimensions were 14 in. height and 18 in. diameter, and the machine held 64 l. of liquor. This machine did not have variable speed drive.

Machine A1—"Agitator type." Similar to Machine A but could be used at two different speeds. The "normal" speed was 75 cycles/min. and the "low" 50 cycles/min.

Machine B—"Agitator type." A central cylinder with three protruding rubber rings gave the washing action by a vertical, reciprocating movement. Two washing speeds were available, 300 cycles/min. and 210 cycles/min.

Machine C—"Agitator type." Six centrally mounted vanes gave the washing action by a rapid eccentric movement of the complete central unit. Two speeds were available, 460 cycles/min. and 200 cycles/min.

Machine D—"Rotating drum type." A cylindrical drum, 19 in. diameter and 11 in. long, mounted on a horizontal axis, rotated in the washing liquor at 58 revs./min. The machine held 15 l. of liquor.

Machine E—"Impeller type." An impeller, about 6 in. diameter with 6 vanes about 0.5 in. high, fitted into the side of the 30-l. bowl. The normal running speed of the impeller (when the bowl is empty) is 710 revs./min., but this could be slowed to 475 revs./min. by changing a driving pulley.

*Shrinkproofing treatments.* Strips of fabric, about 6 in. wide and 3 yd. long, were treated in a laboratory-size, winch dyeing machine to ensure even treatments. Smaller samples, treated with little or no stirring in beakers, did not always give satisfactory results. Treatments studied were permanganate/salt [27], permanganate/hypochlorite [38], permonosulfuric acid followed by sulfite [50], acid chlorination (carried out by adding bromate to acid solutions of saturated salt [27]), hypochlorite at pH 8 [9], peracetic acid/hypochlorite [11], and gaseous chlorination [55]. The procedures used were as given in the original references.

*Estimation of cystine.* This was done polarographically by the method of Stricks, Kolthoff, and Tanaka [51].

*Alkali solubility.* Determined by the method of Harris and Smith [19].

*Bursting strength.* Determined wet and dry [25] on a standard Mullen type testing machine.

*30% Index.* Determined by the method of Speakman [44].

*Friction measurements.* Fabric samples were allowed to stand for 2 hr. in a phosphate-borate buffer at pH 9.0 before fibers were withdrawn for friction measurements. The measurements were made by

**TABLE I. Rate of Felting of Plain-Weave and Plain-Knit Fabrics**

| Fabric No. | Yarn count, tex. | Singles twist, turns/cm. | Twofold twist, turns/cm. | Fabric weight, g./m². | Ends and picks per cm. | Compactness ratio | Stitch length, cm. | Initial rate of felting shrinkage, %/min. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | Machine A* | Machine D* |
| 1 | 2/30 | 3.9 | 3.9 | 107 | 13 × 12 | 0.50 | — | 1.0 | 2.4 |
| 2 | 2/19 | 7.1 | 5.9 | 94 | 13 × 16 | 0.55 | — | 0.4 | 0.7 |
| 3 | 2/22 | 5.9 | 4.7 | 145 | 24 × 22 | 0.81 | — | 0.2 | 0.3 |
| 4 | 2/22 | 5.9 | 4.7 | 114 | 18 × 18 | 0.63 | — | 0.8 | 1.4 |
| 5 | 2/22 | 5.9 | 4.7 | 74 | 12 × 12 | 0.42 | — | 1.1 | 2.2 |
| 6 | 2/37 | 2.8 | 2.4 | 320 | — | — | 0.49 | 0.3 | 0.7 |
| 7 | 2/37 | 2.8 | 2.4 | 205 | — | — | 0.69 | 1.2 | 3.2 |
| 8 | 2/37 | 3.5 | 2.0 | 230 | — | — | 0.62 | 0.9 | 2.8 |
| 9 | 2/19 | 5.9 | 4.3 | 145 | — | — | 0.62 | 1.0 | 3.0 |
| 10 | 2/30† | 2.0 | 2.0 | 332 | — | — | 0.87 | 1.3 | 3.7 |

* 1000 g. load.
† Knitted with two ends up.

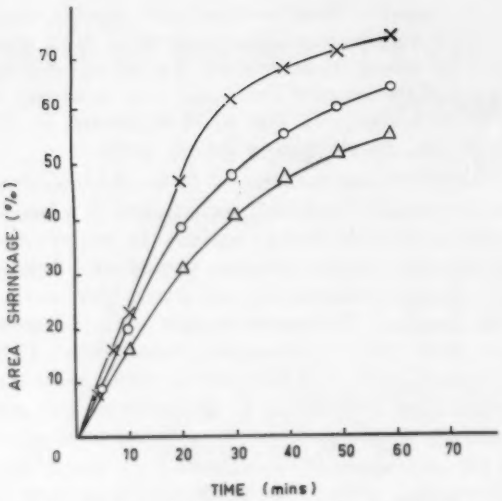



**Fig. 1.** Rate of felting of Fabric 1 in Machine D.

| | Curve | Initial rate, % area shrinkage/min. |
|---|---|---|
| ○ | Without soap | 2.0 |
| × | 0.05% soap | 2.4 |
| △ | 0.3% soap | 1.6 |

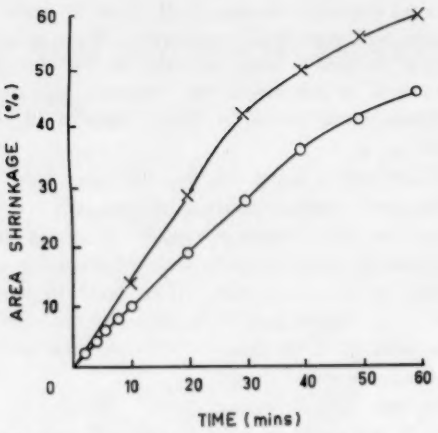



**Fig. 2.** Rate of felting of Fabric 1 in Machine A.

| | Curve | Initial rate, % area shrinkage/min. |
|---|---|---|
| ○ | 1000-g. load | 1.0 |
| × | 3000-g. load | 1.4 |

the capstan method [23], fiber and keratin rod being lubricated with a similar pH 9 buffer containing 0.05% (wt./vol.) Nonion C (a nonionic detergent supplied by Gardinol Chemical Co.). The felting behavior of all samples was found to be the same in this medium as in the soap solutions generally used for the felting tests.

## Results

### *Felting Shrinkage of Untreated Fabrics*

The normal type of shrinkage–time curve has been obtained with the large number of fabrics investigated during the course of this work (Figures 1, 2, 3, 6, 7, 8) i.e., an initial straight line followed by a falling off in rate with time [8, 10, 20, 52]. Any early induction period, as found on milling tests [35], and with a worsted fabric [28, 29], could not be detected in any of our tests, at times of washing down to 1 min. and with an accuracy of about ± 1% actual area shrinkage. Accordingly, our results are expressed simply as initial percent area felting shrinkage per minute, estimated from the slope of the straight part of the graphs.

There is an optimum range of concentration of soap for maximum felting rate in all the machines [see also 8, 54]. A concentration of 0.05% wt./vol. soap is in this range for all machines at the temperature of 45° chosen for this work. Figure 1 illustrates the effect of soap concentration on the felting of Fabric 1 in Machine D. In agitator machines, where the goods are always immersed in the liquor, soap slightly increases the rate of felting but has nowhere near as large an effect as in Machine D [8, 54].

The rate of felting varies considerably in the different machine types, as shown in Figures 1, 2, and 3. Machine A is shown as typical for agitator types on "normal" speed. Initial felting rates, expressed as area shrinkages, of Fabric 1, with 1000-g. loads, are: Machine A, 1.0%/min.; Machine A1, normal speed, 0.8%/min.; Machine A1, low speed, 0.4%/min.; Machine B, normal speed, 1.5%/min.; Machine B, low speed, 1.0%/min.; Machine C, normal speed, 0.7%/min.; Machine C, low speed, 0.2%/min. A convenient simplification is to call two classes of machine, the rotating drum and high-speed impeller, "severe" in their action and the agitators and low-speed impeller, "gentle."

The relative differences for these two types of action on a range of fabric structures are shown in Table I. These structures were chosen from those studied to show extremes of behavior, rather than as a systematic illustration of structure variables. Thus, Fabric 1 shows abnormally rapid felting for

a woven structure while Fabric 3 is very resistant to felting; similarly, Fabrics 6 and 10 are extremes for plain knits, Fabric 6 showing that it is possible to obtain knitted fabrics just as resistant to felting as many wovens. In general, the higher the initial rate of felting, the larger is the difference in rates observed on gentle or severe washing.

The effect of load of goods in the machine is very small when the action is severe, as in Machines D and E. The forces applied in these machines, even at low loads (< 200 g.), may be sufficiently high to be in the range where increasing the force has only a small effect on felting rate [52]. Above a certain critical load in the gentle machines, at normal speeds (about 2.5 kg.), the felting rate increases (Figure 2, Table II). (This could not be demonstrated for Fabrics 2 and 3, or at low agitator speeds, where any increase is possibly within the experimental error of ± 0.1% area shrinkage/min.) This means that the force applied to the fabrics is higher above this critical liquor : goods ratio [2].

*Felting Shrinkage of Shrink-Resistant Fabrics*

The rates of felting of Fabrics 1 and 9, after treatment with various concentrations of permanganate by the permanganate/salt method [27], are given in Figures 4, 5, 6, and 7.

From Figure 4 it can be seen that treatment with 3% permanganate on the weight of wool simply decreases the initial rate of felting of Fabric 1 in Machine D. Such an effect can be obtained in any of three ways: for a given fabric structure, by washing at a different force level, or by chemical treatment, and for given felting conditions, by varying the fabric structure. As the severity of the shrink-proofing treatment is increased, the initial rate of shrinkage is lowered to zero in Machine A and to 0.1–0.2%/min. in Machine D.

**TABLE II. Rate of Felting at Two Different Loads in Agitator Machines**

| Fabric No. | Machine | Initial rate of felting, % area shrinkage/min. 1000-g. load | 3000-g. load |
|---|---|---|---|
| 1 | A normal speed | 1.0 | 1.4 |
| 1 | A1 normal speed | 0.8 | 1.3 |
| 1 | C normal speed | 0.7 | 1.1 |
| 4 | A | 0.8 | 1.0 |
| 5 | A | 1.1 | 1.4 |
| 7 | A | 1.2 | 1.8 |
| 8 | A | 0.9 | 1.2 |
| 9 | A | 1.0 | 1.4 |
| 10 | A | 1.3 | 1.9 |

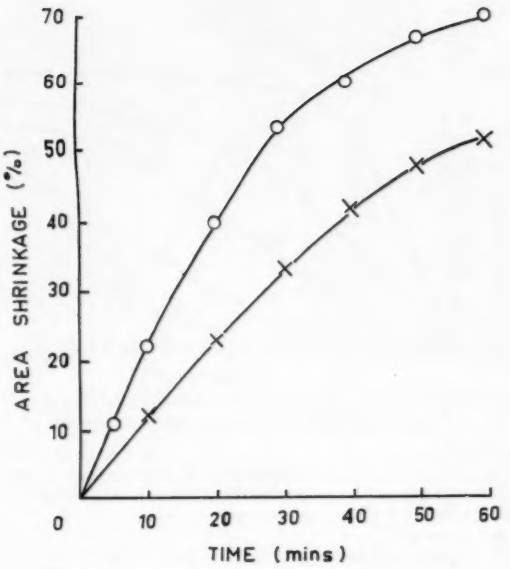



**Fig. 3.** Rate of felting of Fabric 1 in Machine E.

| Curve | Initial rate, % area shrinkage/min. |
|---|---|
| ○ Full speed | 2.2 |
| × Slow speed | 1.2 |

The behavior of treated knitted fabrics could not be assessed accurately due to initial stretching of the knitted structure, which could possibly occur simultaneously with felting (Figures 6 and 7).

The rate of felting increases after a certain time, both this increased rate and the time at which it commences depending on the degree of treatment. Similar behavior has been noted before [7, 12, 45]. However, it is unlikely that this is due to untreated fibers gradually beginning to control the felting rate [7] as a result of the wool having been unevenly treated, since microscopical examination of treated yarns, still containing manganese dioxide, showed even deposits over each fiber. Also, carefully treated tops, where treatment was almost certainly even, show exactly the same behavior when made into similar structures. The effect of concentration is, therefore, probably not due simply to treating more fibers as concentration is increased.

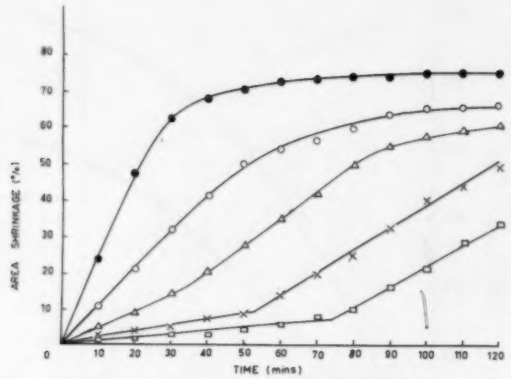



**Fig. 4.** Rate of felting in Machine D of Fabric 1 after treatment with permanganate/salt.

| Curve | Initial rate, % area shrinkage/min. | Rate of second stage, % area shrinkage/min. |
|---|---|---|
| ● Untreated | 2.4 | — |
| ○ 3% permanganate | 1.1 | — |
| △ 4% permanganate | 0.4 | 0.7 |
| × 5% permanganate | 0.2 | 0.6 |
| □ 6% permanganate | 0.1 | 0.6 |

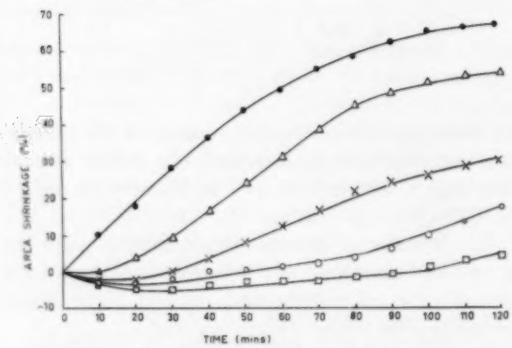



**Fig. 5.** Rate of felting in Machine A of Fabric 1 after treatment with permanganate/salt.

| Curve | Initial rate, % area shrinkage/min. | Rate of second stage, % area shrinkage/min. |
|---|---|---|
| ● Untreated | 1.0 | — |
| △ 1% permanganate | 0 | 0.8 |
| × 2% permanganate | uncertain | 0.4 |
| ○ 3% permanganate | uncertain | 0.3 |
| □ 4% permanganate | uncertain | not measured |

The other industrial treatments studied all give similar shrinkage–time curves when fabric is treated to give an equivalent degree of shrink resistance. The full curves are only given in detail for one treatment (e.g., Figure 4), but the concentrations of other

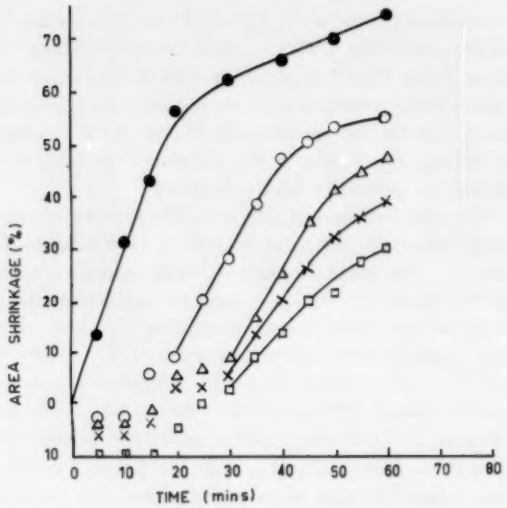



**Fig. 6.** Rate of felting in Machine D of Fabric 9 after treatment with permanganate/salt.

| Curve | Initial rate, % area shrinkage/min. | Rate of second stage, % area shrinkage/min. |
|---|---|---|
| ● Untreated | 3.0 | — |
| ○ 3% permanganate | uncertain | 1.9 |
| △ 4% permanganate | uncertain | 1.6 |
| × 5% permanganate | uncertain | 1.2 |
| □ 6% permanganate | uncertain | 1.0 |

reagents which will produce almost identical curves are given in Table III. All these methods are capable of producing adequately shrink-resistant wool with little adverse effect on other properties (Tables III and IV) [27].

The importance of defining washing conditions when presenting results on tests for shrink resistance is shown by results such as given in Figure 8. In a 60-min. wash, treated Fabric 10 had shrunk 1% in Machine A (1000-g. load) and 50% in Machine D, compared with 63% and 71%, respectively, for untreated samples. If standard washing times are chosen for testing, therefore, the force level applied must be indicated in some way. A felting rate of the untreated fabric compared with that of a standard fabric could be a satisfactory way of doing this.

When the shrinkage of treated fabric is compared with a given shrinkage of untreated fabrics, different conclusions could again be drawn from tests in different machines. For example, for 40% shrinkage of untreated Fabric 10, the treated fabric shrank zero and 4% in Machines A and D, respectively

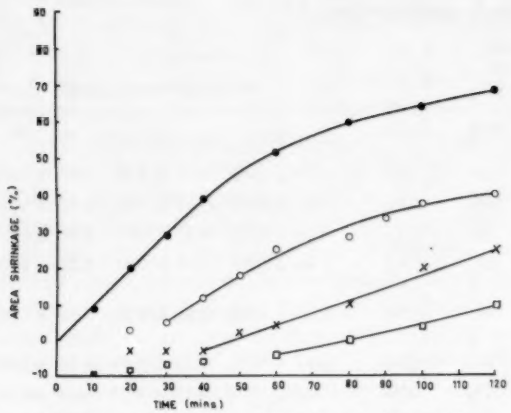



**Fig. 7.** Rate of felting in Machine A of Fabric 9 after treatment with permanganate/salt.

| Curve | Initial rate, % area shrinkage/min. | Rate of second stage, % area shrinkage/min. |
|---|---|---|
| ● Untreated | 1.0 | — |
| ○ 2% permanganate | uncertain | 0.7 |
| × 3% permanganate | uncertain | 0.4 |
| □ 4% permanganate | uncertain | 0.3 |

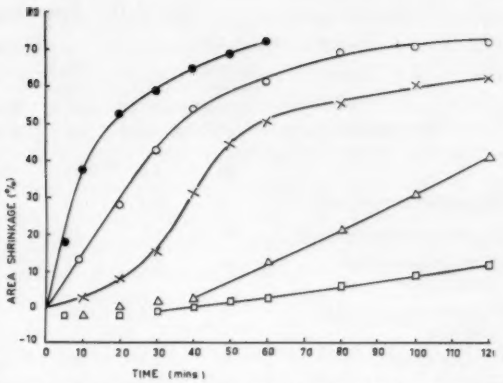



**Fig. 8.** Rates of felting of Fabric 10, untreated and treated with permanganate/salt, in Machines A and D.

| Curve | Initial rate, % area shrinkage/min. | Rate of second stage, % area shrinkage/min. |
|---|---|---|
| ● Untreated, Machine D | 3.7 | — |
| ○ Untreated, Machine A | 1.3 | — |
| × 5% permanganate, Machine D | 0.4 | 1.6 |
| □ 5% permanganate, Machine A, 1000-g. load | uncertain | 0.2 |
| △ 5% permanganate, Machine A, 3000-g. load | uncertain | 0.4 |

(1000-g. loads), but for 60% shrinkage for untreated, the treated fabric shrank 1% or 18% respectively. This treated fabric is completely shrinkproofed on washing at low agitator speeds, no felting being detectable after washing for 4 hr.

*Properties of Shrink-Resistant Wool*

Table IV gives results of a variety of tests carried out on wool from Fabric 1 treated by different industrial shrinkproofing methods.

The cystine loss, change in alkali solubility, change in elastic properties (including resilience [43]) are all about the same for the different treatments. These changes can also, of course, be brought about with many other reagents which do not affect the felting property, and so cannot in themselves account for shrinkproofing.

Change in frictional properties, especially lowering the difference between $\mu_2$ (the anti-scale frictional coefficient) and $\mu_1$ (the with-scale frictional coefficient), is usually considered to be a major factor in reducing felting rate by chemical treatment (e.g., see [1, 36] for reviews). All the treatments in Table IV reduce $(\mu_2 - \mu_1)$, but, for a given degree of

**TABLE III. Concentrations of Reagents Required to Give Equivalent Degrees of Shrink Resistance on Fabric 1**

| Concentration reagent used, % on wt. wool | | | | | |
|---|---|---|---|---|---|
| Permanganate/salt | Permono-sulfuric acid | Acid chlorine | Permanganate +chlorine* | Peracetic acid +chlorine* | Area shrinkage in Machine D, % |
| — | — | — | — | — | 60 |
| 3 | 1.0 | 1.3 | 0.8 + 0.8 | 1.0 + 1.8 | 30 |
| 4 | 1.5 | 1.8 | 1.3 + 1.3 | 1.0 + 2.3 | 13 |
| 5 | 2.0 | 2.2 | 1.8 + 1.8 | 1.0 + 2.8 | 5 |
| 6 | 2.4 | 2.6 | 2.2 + 2.2 | 1.0 + 3.2 | 3 |

* "Chlorine" means the quantity of active chlorine in the hypochlorite solution added.

**TABLE IV. Properties of Shrink-Resistant Fabric 1**

| Treatment | Area shrinkage Machine D, % | Cystine, mole/$10^4$ g. wool | Alkali solubility, % | Bursting strength | | 30% index | Frictional coefficients‡ | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Conditioned* | Wet | | $\mu_2$ | $\mu_1$ | $\mu_2 - \mu_1$ |
| — | 40 | 4.6 | 12 | 114 | 86 | 1.00 | 0.52 ± 0.02 | 0.23 ± 0.01 | 0.29 ± 0.02 |
| 5% permanganate/salt | 3 | 4.3 | 18 | 108 | 81 | 0.94 | 0.49 ± 0.02 | 0.31 ± 0.02 | 0.18 ± 0.03 |
| 5% permanganate/water | 30 | 4.3 | 19 | 110 | 80 | 0.94 | 0.50 ± 0.02 | 0.30 ± 0.02 | 0.20 ± 0.03 |
| 2% permonosulfuric acid/sulfite | 4 | 4.2 | 21 | 111 | 82 | 0.93 | 0.46 ± 0.02 | 0.24 ± 0.01 | 0.22 ± 0.02 |
| 2% permanganate/2% chlorine† | 3 | 4.2 | 20 | 108 | 79 | 0.94 | 0.47 ± 0.02 | 0.36 ± 0.02 | 0.11 ± 0.03 |
| 2% acid chlorine | 5 | 4.3 | 17 | 114 | 86 | 0.93 | 0.47 ± 0.02 | 0.30 ± 0.02 | 0.17 ± 0.03 |
| 6% chlorine at pH 8† | 5 | 4.2 | 21 | 107 | 78 | 0.94 | 0.45 ± 0.02 | 0.27 ± 0.02 | 0.18 ± 0.03 |
| 1.5% gaseous chlorine | 4 | 4.3 | 17 | 115 | 87 | 0.95 | 0.56 ± 0.03 | 0.46 ± 0.02 | 0.10 ± 0.04 |
| 1% peracetic acid/3% chlorine† | 5 | 4.2 | 20 | 109 | 81 | 0.94 | 0.49 ± 0.02 | 0.30 ± 0.02 | 0.19 ± 0.03 |

* Conditioned at 20° and 65% RH
† "Chlorine" means the quantity of active chlorine in the hypochlorite solution added.
‡ Values given are means and standard deviations from measurements on at least 15 fibers.

shrink resistance, $(\mu_2 - \mu_1)$ varies from 0.10 to 0.22. Also, permanganate/water and permanganate/salt treatments have the same effect on frictional properties, yet the latter, but not the former, has given adequate shrink resistance [26]. (It is of interest that microscopic examination of cross-sections indicates that manganese dioxide is deposited solely on the surface during both treatments, but this evidence for "surface reaction" is in contrast to other measurements given in Table IV which show that reaction probably has occurred throughout fibers in both cases.) These results show that there is no direct relation between felting and $(\mu_2 - \mu_1)$, as measured here, for the different treatments.

Treatments which reduce $(\mu_2 - \mu_1)$ the most are those which increase $\mu_1$ most. If an increase in the actual values of the coefficients played a part in reducing felting this behavior might be expected to be reversed; that is, for a given degree of shrink resistance, the actual coefficients should be increased most when $(\mu_2 - \mu_1)$ is lowered least.

Some of the results in Table IV are qualitatively different from those found with Lincoln 36's fibers [6, 26] when identical techniques of treatment and measurement were used. For example, acid chlorination increased $\mu_1$ and $\mu_2$ very markedly on Lincoln, but on Merino, $\mu_2$ is reduced and $\mu_1$ increased. The value of $(\mu_2 - \mu_1)$ for untreated Lincoln fibers is 0.14, but some of the treated Merino fibers have a much higher $(\mu_2 - \mu_1)$ and felt more slowly.

Discrepancies in the literature have been discussed before [e.g., 16] and can easily be noted by comparing results from the large number of published papers on this aspect of shrinkproofing [e.g., 1, 6, 14, 16, 22, 23, 24, 31, 33]. The results must still therefore be regarded with some doubt and it may well be that some of the friction work carried out has not measured a fundamental property of untreated or treated wool. A clear relationship has not yet been established between frictional properties and rate of felting of different wools treated with each of the variety of effective reagents.

It has been suggested that friction is related to handle of wool [27, 34] but the present results are against this. For example, permanganate/hypochlorite-treated wool is softer than acid chlorinated (which is harsher than untreated), but the frictional coefficients are about the same.

## Discussion

The effect of fabric structure on the rate of felting of untreated wool indicated here has been well established by previous systematic work [3, 5, 13, 15, 17, 20, 52]. The results are as expected. The lower the yarn twist, the looser the fabric, or the higher the applied mechanical force [52], the greater

is the rate of felting. This has been explained [52, 53] by considering the frictional resistance of fibers to the movements leading to felting. The resistance is increased by increasing the number of fiber contacts, by varying the structure as described, while in a given structure, the resistance to movement is overcome more quickly by higher applied forces.

Wool, after treatment with any of the chemical shrinkproofing methods studied, gives similar shrinkage–time curves. The initial rate of felting is decreased almost to zero but a second stage starts after certain times, depending on the degree of treatment, when felting occurs much more rapidly. The second stage of the curves is similar to the complete curve of untreated wool, with an initial straight line, followed by a slowly decreasing rate of felting. The initial rate of felting during the second stage is lower for treated wool than untreated, all other factors being constant.

The present results indicate that the shrinkage–time curves describe the fundamental behavior of wool made shrink-resistant by chemical treatments. It would be misleading, therefore, to speak of the second stage of the curves as a "shrinkage-resistance breakdown" [e.g., 7], since this implies that uneven treatments are necessarily obtained or that the felting property is in some way restored to the treated fibers, a most unlikely happening.

Makinson [28, 29] has shown that, in the initial stages of felting of a worsted fabric, lengths of fibers move rootwards and eventually produce loops on the front parts. When the loops are sufficiently large, entanglements begin to occur and measurable felting begins. We have not been able to find any such delay in the start of felting of untreated fabrics in washing machines, but it is possible that this is too rapid to be detected by the methods used. It could be, then, that the shrinkage–time curves of treated fabrics do actually belong to the same family as those of untreated fabrics, although it is still possible that felting occurs by a different mechanism in treated fabrics.

If the first postulate is correct, then the shrinkproofing treatments affect both parts of the curve—the small, longitudinal fiber movements which are definitely reduced by chemical treatment [28] as well as the more rapid movements associated with fiber entanglement. It is entirely reasonable on this basis that either increased frictional coefficients, or a reduced difference between $\mu_2$ and $\mu_1$, should lead to the observed behavior of treated fabrics. However, a general quantitative relationship has not been established between frictional properties and rates of felting, although it appears to have been in one case [53]. It is equally possible that other properties of the fibers, such as compressibility, resistance to, or recovery from, bending [31] could be affected by the shrinkproofing treatments and lead to the same shrinkage–time curves. A demonstration of the actual mode of action of the treatments still awaits satisfactory experimental measurement of all the possible important fiber properties.

Of practical importance are the results emphasizing again that it is difficult to treat loosely knitted wool fabrics so that they give satisfactory performance in both gentle and severe washings. If treated so that very little felting occurs on severe laundering, undesirable stretching will occur on gentle washing. If treated at a lower level to give complete satisfaction in gentle washing, felting will occur quite rapidly under severe conditions. The usefulness of modern, low-speed home washing machines [2] for laundering of woolen garments is clearly demonstrated.

## Acknowledgments

I am grateful to Dr. M. Lipson, Dr. A. J. Farnworth, and Mrs. K. R. Makinson for discussion and to Mr. H. D. Feldtman, Mrs. K. L. Wright and Miss J. L. Barnett for assistance with the experimental work.

## Literature Cited

1. Alexander, P. and Hudson, R. F., "Wool; Its Chemistry and Physics," London, Chapman and Hall Ltd., 1954, p. 25.
2. Bogaty, H. and Harris, H. E., *Am. Dyestuff Reptr.* **47**, 369 (1958).
3. Bogaty, H., Lourigan, G. H., and Harris, H. E., TEXTILE RESEARCH JOURNAL **28**, 733 (1958).
4. Bogaty, H., Sookne, A. M., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 822 (1951).
5. Bogaty, H., Weiner, L. I., Sookne, A. M., Cozart, M. L., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 895 (1951).
6. Bradbury, J. H., *J. Textile Inst.* **51**, T1226 (1960).
7. Carter, E. G. H., "Fibrous Proteins, a Symposium," Society of Dyers and Colourists, 1946, p. 201.
8. Carter, E. G. H. and Grieve, W. S. M., W.I.R.A. Special Publication No. 6 (1944).
9. Clapham, H. F., Harris, M., and Smith, A. L., U. S. Patent 2,457,033 (1948).
10. le Compte, G. C. and Creely, J. W., *Am. Dyestuff Reptr.* **29**, 387 (1940).

11. Davidson, A. N. and Preston, R., *J. Textile Inst.* **47**, P685 (1956).
12. Dominik, M., *Melliand Textilber.* **41**, 875 (1960).
13. Dutton, W. A., *J. Soc. Dyers Colourists* **60**, 293 (1944).
14. Farnworth, A. J., submitted to *J. Soc. Dyers Colourists.*
15. Farnworth, A. J., Lipson, M., and McPhee, J. R., *J. Textile Inst.* **51**, T1504 (1960).
16. Freney, M. R., "Fibrous Proteins, a Symposium," Society of Dyers and Colourists, 1946, p. 178.
17. Freney, M. R. and Lipson, M., *J. Council Sci. Ind. Research* **14**, 25 (1941).
18. Graham, D. R. and Statham, K. W., *J. Soc. Dyers Colourists* **75**, 386 (1959).
19. Harris, M. and Smith, A. L., *J. Research Nat. Bur. Standards* **17**, 577 (1936).
20. Johnson, A., *J. Textile Inst.* **29**, T7 (1938).
21. King, A. T., *Wool Record* **52**, 1265 (1937).
22. Lindberg, J. and Gralén, N., TEXTILE RESEARCH JOURNAL **19**, 183 (1949).
23. Lipson, M. and Howard, P., *J. Proc. Roy. Soc. N. S. Wales* **79**, 92 (1946).
24. Lohani, B. K., Valentine, L., and Whewell, C. S., *J. Textile Inst.* **49**, T265 (1958).
25. McPhee, J. R., TEXTILE RESEARCH JOURNAL **29**, 303 (1959).
26. McPhee, J. R., TEXTILE RESEARCH JOURNAL **30**, 349 (1960).
27. McPhee, J. R., TEXTILE RESEARCH JOURNAL **30**, 358 (1960).
28. Makinson, K. R., TEXTILE RESEARCH JOURNAL **29**, 431 (1959).
29. Makinson, K. R., TEXTILE RESEARCH JOURNAL **29**, 439 (1959).
30. Makinson, K. R., TEXTILE RESEARCH JOURNAL **30**, 598 (1960).
31. Martin, A. J. P., *J. Soc. Dyers Colourists* **60**, 325 (1944).
32. Mercer, E. H., *J. Council Sci. Ind. Research* **15**, 285 (1942).
33. Mercer, E. H., *Nature* **155**, 573 (1945).
34. Mercer, E. H. and Makinson, K. R., *J. Council Sci. Ind. Research* **19**, 200 (1946).
35. Moncrieff, R. W., "Wool Shrinkage and Its Prevention," London, National Trade Press Ltd., 1953, p. 110.
36. Moncrieff, R. W., "Wool Shrinkage and Its Prevention," London, National Trade Press Ltd., 1953, p. 434.
37. Munden, D. L., *J. Textile Inst.* **50**, T448 (1959).
38. Raynes, J. L., Stevenson, F. M., and Stevensons (Dyers) Ltd., British Patent 569,730 (1945).
39. Schofield, J., *J. Textile Inst.* **29**, T246 (1938).
40. Schofield, J., *J. Textile Inst.* **33**, T181 (1942).
41. Schofield, J., *J. Soc. Dyers Colourists* **61**, 77 (1945).
42. Sookne, A. M., Bogaty, H., and Harris, M., TEXTILE RESEARCH JOURNAL **20**, 637 (1950).
43. Sookne, A. M., Bogaty, H., and Harris, M., TEXTILE RESEARCH JOURNAL **21**, 827 (1951).
44. Speakman, J. B., *J. Textile Inst.* **38**, T102 (1947).
45. Speakman, J. B., Chamberlain, N. H., and Menkart, J., *J. Textile Inst.* **36**, T91 (1945).
46. Speakman, J. B. and Goodings, A. C., *J. Textile Inst.* **17**, T607 (1926).
47. Speakman, J. B., Menkart, J., and Liu, W. T., *J. Textile Inst.* **35**, T41 (1944).
48. Speakman, J. B. and Stott, E., *J. Textile Inst.* **22**, T339 (1931).
49. Speakman, J. B., Stott, E., and Chang, H., *J. Textile Inst.* **24**, T273 (1933).
50. Stevensons (Dyers) Ltd. and Fell, E. T., British Patent 716,806 (1954).
51. Stricks, W., Kolthoff, I. M., and Tanaka, N., *Anal. Chem.* **26**, 299 (1954).
52. van der Vegt, A. K. and Schuringa, G. J., TEXTILE RESEARCH JOURNAL **24**, 99 (1954).
53. van der Vegt, A. K. and Schuringa, G. J., TEXTILE RESEARCH JOURNAL **26**, 9 (1956).
54. Weiner, L. I., "Quartermaster Corps Accelerated Test Method for Evaluating Shrinkresistant Wool as Developed for 10½ oz. Wool Shirting," Office of the Quartermaster General, Textile Series Report No. 53 (1948).
55. Wool Industries Research Association, King, A. T., and Galley, R. A. E., British Patent 417,719 (1933).

*Manuscript received January 23, 1961.*

# The Use of Unheated Air in the Drying of Wool

**J. G. Downes and G. B. McMahon**

*C.S.I.R.O. Wool Research Laboratories, Division of Textile Physics, Ryde, N.S.W., Australia*

**Abstract**

In drying wool by forced air flow to a uniform regain in the range 8% to 16%, the amount of water removed per unit volume of air used is almost independent of the air temperature. In view of this, the paper examines the practicability and economics of using unheated air for wool drying. Running costs depend on the atmospheric humidity at the location of the dryer, but usually are appreciably lower than those of an efficient steam-heated dryer. The air intake per pound of water removed is much greater than in conventional dryers but the blower power required is approximately the same. No circulation is used, and this permits close control of the regain of the wool leaving the dryer.

## Introduction

If a mass of wet wool is to be brought to a uniformly air-dry state at some desired value of regain by blowing air through it, then the relative humidity of the air used must have the value which is in equilibrium with wool of that condition. (Processes involving overdrying are not considered here.) A study [6], made under these conditions, of how the drying capacity of the air (i.e., the amount of water removed per unit volume of ingoing air) depends on its temperature shows that when wool is being dried to a regain in the range 8–16%, as is commonly required, little or no increase in capacity is gained by raising the temperature above the ambient. This is illustrated by the curve of Figure 1, which shows the relationship between capacity and temperature when the wool is to be left at a regain of 16%. It is a commonly held view that heating of the air is desirable in dryers; but if this is so, other factors are being brought into consideration, namely: (i) that overdrying of some or all of the wool is permitted (this is not necessarily disadvantageous since it can provide the basis of rapid drying methods giving a desired value for *average regain*, but such methods are outside the scope of this paper); (ii) that recirculation of the drying air is required; or (iii) that increased temperature is necessary to accelerate diffusion of water from within the fibers or around them where the forced convection is ineffective.

It seems worth while to investigate the practicability of a dryer design based on the use of unheated air, in view of the possible saving of heat energy; this paper describes the results of such a study [5].

## Basis of Dryer Design

We shall assume that the wool to be dried is uniform in density of packing and arranged in a layer of uniform thickness, and that all the drying air is made to flow through this layer. We shall apply in the first instance the theory developed by Cassie and others [1, 2, 3, 4, 7] for the flow of air through a mass of hygroscopic fibers. According to this theory a "drying front" moves through the layer from the upstream face, the wool behind the front being in equilibrium with the incoming air, while beyond the front it is at its initial regain. The theory as developed is concerned only with fibers at regains below the saturation value, but it can be extended quite readily to the case where liquid water is present within the mass. In this case the emerging air is saturated and at the wet-bulb temperature of the incoming air; it remains so until the front emerges at the downstream face, at which time the mass is in equilibrium with the ingoing air. The speed with which the front advances is proportional to, but much less than, the speed of the air flow and depends also on the water-carrying capacity of the ingoing air and the amount of water to be removed from the mass.

As a starting point we shall assume the ambient air to have the standard condition of 65% RH and 20° C. temperature (i.e., a wet-bulb depression of 4.2° C.). Wool brought from the wet state into equilibrium with this air will have a regain of about 16.5%. For the assumed atmospheric conditions the water content of the ingoing air will be 11.1 g./m.$^3$; the wet-bulb temperature of this air is 15.8° C. and the outgoing air, being saturated at this temperature,

will have a water content of 13.3 g./m.$^3$. The amount of water removed from the wool per unit volume of air flowing will therefore be 2.2 g./m.$^3$.

In general the amount of water removed per unit volume of air flowing is proportionate to the value of wet-bulb depression of the drying air.

The only energy required in the dryer design now proposed is that required to force the air through the wool, and a question of interest is whether this energy is comparable in cost with the heat energy used in drying the same amount of wool by conventional means. If a pressure, $p$, is required to force a volume of air, $V$, through the mass, then the work done is $pV$, and the work per unit volume is simply $p$. If $m$ denotes the amount of water removed per unit volume of air flowing, then $m/p$ is the amount of water removed per unit of work done and is therefore a measure of the efficiency of the drying process. The required pressure, $p$, depends on the density of packing of the wool, the thickness, $t$, of the layer, the area, $a$, of the layer normal to the flow, and the volume rate of flow, $v$, according to the relation

$$p = \frac{vkt}{a} \tag{1}$$

where $k$ is the measure of the resistance to air flow. $k$ is expressed in terms of pressure drop per unit volume rate of flow through a unit cube of wool, or in what is equivalent, pressure drop per unit air velocity through unit thickness; it is a function only of packing density and fiber diameter. We have then for the efficiency

$$\frac{m}{p} = \frac{am}{vkt} = \frac{m^2a}{Mkt} \tag{2}$$

where $M = mv$ = rate of removal of water. Hence for given throughput, packing density, mean fiber diameter, and atmospheric conditions (i.e., $M$, $k$, and $m$ fixed) the efficiency of the dryer depends directly on the area of the wool layer being dried and inversely on its thickness.

To assess quantitatively the efficiency of a dryer of the proposed design we require data on the resistance, $k$, of the wool to air flow. Measurements have been made at room conditions of pressure drop and air flow through samples of Merino wool (21$\mu$ average diameter) [1] packed to various densities, from which values of $k$ may be derived; these are plotted in the curve of Figure 2. As an example, let us estimate the efficiency of a dryer which is to have an output of 800 lb. of wool per hour at a regain of 16%. We shall assume the air is at the standard condition specified earlier. With normal squeeze-rolling, the input of wet wool to the dryer will be at a regain of about 65% so that 345 lb./hr. (43.5 g./sec.) is the required rate of water removal, $M$. We shall further assume a layer thickness of 5 cm., a packing density of 0.05 g./cm.$^3$ (this corresponds to lightly compressed wool) and a dryer 30 ft. long by 4 ft. wide (area of layer 120 ft.$^2$ or $1.11 \times 10^5$ cm.$^2$). Then from Equation 2 and Figure 2 we find that efficiency

$$= \frac{m}{p} = \frac{m^2a}{Mkt}$$

$$= \frac{(2.2 \times 10^{-6})^2 \times 1.11 \times 10^5}{43.5 \times 5.7 \times 5} \text{ g./erg}$$

$$= 4.35 \times 10^{-10} \text{ g./erg}$$

$$= 1.01 \times 10^{-2} \text{ lb./B.T.U.}$$

By comparison, the most efficient hot-air dryers now available are quoted as having a steam consumption of about 1.5 lb. per pound of water removed, i.e., 1.5 g. steam per gram of water, so that such dryers, even when the energy for their fans is excluded, have an efficiency of only $0.3 \times 10^{-10}$ g./erg, or $6.9 \times 10^{-4}$ lb./B.T.U. On an energy basis the unheated-air dryer is thus seen to be far higher in efficiency (about 14 times better) than a conventional hot-air dryer. However, in terms of operating cost the difference between the two types of dryer is not as great, because of the much lower cost of heat energy (as steam) compared with electrical energy (for the fans). To assess operating costs of the two systems we have assumed some energy costs which are representative of Australian conditions: for electrical energy (purchased) 3d. per kw.-hr. ($8.8 \times 10^{-4}$d. per B.T.U.) and for steam (generated) 19s.[2] per 1,000 lb. ($2.4 \times 10^{-4}$ d. per B.T.U.). Assuming a fan efficiency of 60% for the unheated-air dryer, the running cost is found to be 0.15d. per lb. of water removed, while for an efficient hot-air dryer of conventional type it is 0.43d./lb. (0.35d. steam cost plus 0.08d. blower cost), i.e., 3 times as great.

[1] The variation in $k$ as between dry and wet wool is small enough to be neglected for practical purposes.

[2] Includes operation, maintenance and depreciation of steam plant.

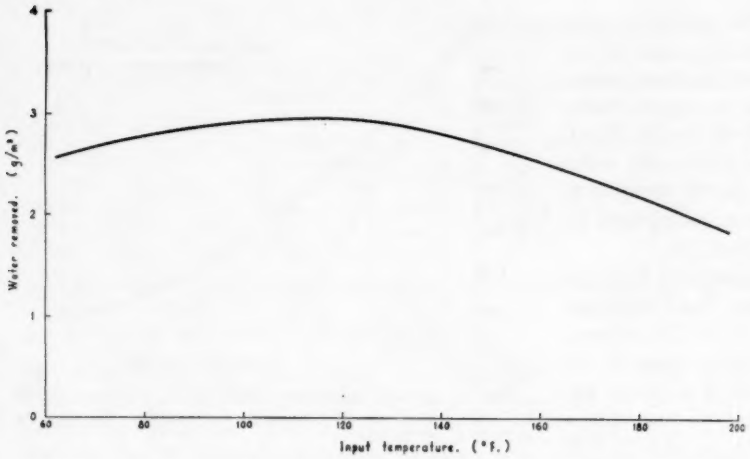



**Fig. 1.** Relationship between the temperature of air and its capacity for removing water, the wool being left at a regain of 16%.

(Where the relative costs of steam and electricity differ markedly from those assumed, comparisons will of course be correspondingly affected.)

The foregoing calculations show that under the assumed conditions a dryer using unheated air and of size comparable to that of a conventional dryer having the same output compares very favorably with the latter in operating costs. In practice there will be departures from the assumed conditions, some of which will increase the operating costs of the unheated-air dryer, and these will now be considered.

It has been assumed that air leaving the wool layer is saturated and remains so throughout the drying process until the "drying front" emerges abruptly at the downstream face, after which the outgoing air is in the same condition as the ingoing air. In practice the emergence of the front is not usually abrupt and the average rate of water removal is less than predicted in the ideal case, for the following reasons:

1. The density of packing will not be completely uniform throughout the layer; in some parts the wool will be less densely packed than in others and air will flow preferentially there, an effect described as "channelling." In these regions the drying front will pass more rapidly through the layer. The air emerging from the layer will consequently after a time be a mixture of saturated and unsaturated air, and must therefore itself be below saturation point.

2. The liquid water in the wool will not be uniformly distributed and may appear both as a thin film on the fiber surfaces, and on and between fibers as droplets. The droplets will be slower to evaporate; after a time they will represent the greater part of the water present and may not be capable of saturating the flowing air.

3. Finally, the "front" theory which we have adopted is a simplified one, in which it is assumed that the wool regain at any point is always in equilibrium with the humidity of the air there. It has been

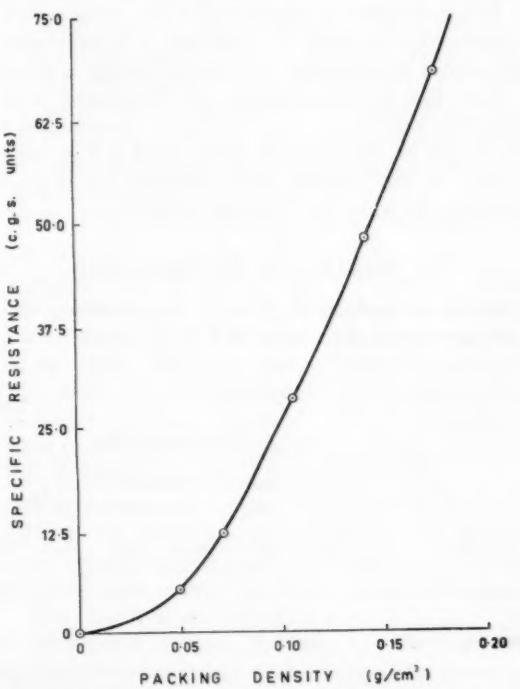



**Fig. 2.** Specific resistance (pressure drop per unit air velocity through unit thickness) to air flow of Merino wool (21$\mu$ mean diameter) at room conditions.

shown [8] that at regains below the saturation value this assumption is not strictly valid, because of the finite time required by water to diffuse from within the wool fibers. The effect is that at regains below saturation the front at any point is no longer abrupt, but has a finite slope. For this reason the water content of the emerging air will not fall abruptly to its final value, but rather at a rate determined by the finite slope of the emerging front.

To assess the effect of these departures from the ideal case a number of tests have been made on the rate of drying of wool beds 2 ft. by 2 ft. in area, packed to various depths and with a range of air speeds. Figure 3 shows the result of a typical experiment in which 2720 g. of wet wool packed to a depth of about 10 cm. was dried by air of 57% RH at 18.5° C., flowing at a rate of 23 m.³/min. The rate of water removal predicted by theory is 2.4 g./m.³. Figure 3 shows that the weight falls at about this rate initially, but more slowly as drying proceeds. The average rate over the time required to dry to 22% regain was 1.1 g./m.³, i.e., 46% of the theoretical rate.

Using this latter figure to adjust the previous calculations for the assumed ideal case, it is found that the energy efficiency for unheated-air drying is about 7 times that for steam drying, and the running costs are about two-thirds those for steam. Improvement in control of regain of the dried wool and in wool quality is also possible when unheated air is used and may increase the economic advantage.

### The Humidity of the Atmosphere

In the example worked out in the preceding section a wet-bulb depression of 4.2° C. was assumed.

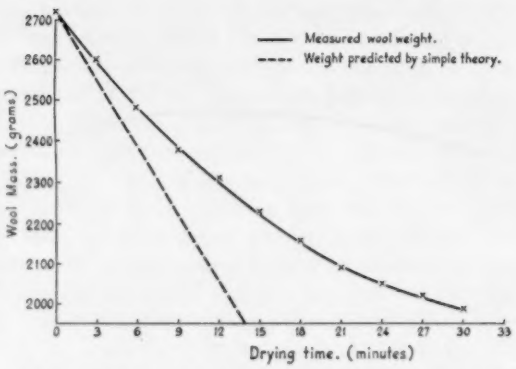



**Fig. 3.** Drying curve for a sample of wet wool (2720 g.) with forced air flow through the sample. Ingoing air at 18.5° C., 57% RH.

It is necessary to examine how the process is affected by air having other values of depression. If the depression is less than 4.2° C. then the capacity of the air to remove water from the wool is reduced and the wool will be left at a higher regain; in both respects the opposite is true if the air has a depression greater than 4.2° C. As an example, for the case of air of depression 2.3° C. (e.g., 20° C. dry-bulb temperature, 80% RH), blown through wet wool and emerging saturated, water is removed at a rate of 1.25 g./m.³ of air flowing (as compared with the figure previously derived of 2.2 g./m.³ for air of depression 4.2° C.), and the wool is left at a regain of 20%.

We can assume that it would be desirable to operate the unheated-air dryer so that its output would at all times have some standard value of regain. To achieve this it would be necessary to control the depression of the ingoing air. On days of

**TABLE I**

| Place | Temperatures, deg. F. | | | | | | Geographical situation | Rainfall | |
|---|---|---|---|---|---|---|---|---|---|
| | Summer average | | Winter average | | Extreme | | | Annual amount, in. | Distribution throughout year |
| | Max. | Min. | Max. | Min. | Max. | Min. | | | |
| Bourke, N.S.W. | 97 | 68 | 66 | 42 | 125 | 25 | Flat inland plain, 400 miles from eastern seaboard. | 11 | Even |
| Sydney, N.S.W. | 78 | 65 | 63 | 47 | 114 | 36 | Eastern seaboard, backed by coastal range of 3,000–4,000 feet. | 45 | Minimum in spring. Maximum in autumn |
| Hobart, Tas. | 69 | 52 | 54 | 41 | 105 | 28 | Eastern seaboard, backed by mountain plateau. | 25 | Even |

TABLE II

| Location | Assumed hours of operation | Proportion of operating time for which heating required | Mean rise in air temperature required during heating periods, deg. F. | Maximum temperature rise required, deg. F.* | Cost, pence per lb. of water removed | | |
|---|---|---|---|---|---|---|---|
| | | | | | Heating | Power for fans | Total |
| Bourke, N.S.W. | 7:30 a.m.–4:30 p.m. | 24% | 6.63 | 15.3 | .10 | .30 | .40 |
| Sydney, N.S.W. | 6:30 a.m.–5:30 p.m. | 58% | 5.9 | 16 | .22 | .30 | .52 |
| Hobart, Tas. | 7:30 a.m.–4:30 p.m. | 61% | 7.55 | 20 | .28 | .30 | .58 |

* This figure is quoted to show the maximum capacity required of the heating installation.

high depression, water vapor would be added; this could easily be done by recirculating some of the saturated outgoing air. On days when the depression was low, it would be necessary to increase it. Two practical means of doing this are to remove water by condensation, or to heat the air.

Condensation is an efficient process but requires a large plant. Heating of the air to increase the depression is inefficient in the sense that the heat put into the air is exhausted and wasted. On the other hand, the necessary heating installation is simple and cheap and may be operated from the steam supply normally available in the mill. To examine the costs of air heating we take the case where the air at 20° C. is to be increased in depression from 2.3° to 4.2° C. This necessitates heating it to 22.9° C., the heat required being 840 cal./m.$^3$. If we take 1.0 g./m.$^3$ as a practically attainable figure for water removal, the heat requirement is 840 cal. per gram of water removed (1510 B.T.U./lb., or 1.57 lb. steam per lb. of water removed). Assuming the heat to be supplied by steam at the cost previously quoted, the price of heating works out at 0.36d. per pound of water removed, i.e., slightly higher than that estimated for an efficient dryer of conventional type.

The preceding example shows that only under very humid conditions is the operating cost of an unheated-air dryer likely to exceed that of a conventional dryer, but how much of the potential efficiency of the unheated-air design can be realized depends on the average ambient depression at the location of the dryer. Since we are assuming that the dryer is producing wool at standard regain no advantage can be taken of the high water-carrying capacity of the air at times of high depression, and the operating costs of the dryer depend on the fraction of the total running time for which the depression is less than some standard figure.

To obtain some indication of how climatic conditions can affect the dryer performance, meteorological data have been analyzed for three locations on the Australian continent, representing two extreme conditions and one intermediate. The climatic conditions at the three locations are summarized in Table I.

The method of analysis was as follows. A value of wet-bulb depression was selected which gave an acceptable compromise between values for the water-removing capacity of the air and the regain at which the wool would be left. There is a close correspondence between wet-bulb depression and regain (particularly for regains over approximately 12%) which is nearly independent of dry-bulb temperature; see for example Downes and McMahon [6]. The value of depression chosen was 4.4° C., i.e., 8° F. (this value corresponds to a relative humidity of 62% at 20° C. dry-bulb temperature), and the corresponding regain is approximately 16%.

For each location the average value was found for the proportion of time in a working day during which the wet-bulb depression was less than the chosen value. This was done by taking a representative sample from meteorological records over a period of 5 years of hourly dry- and wet-bulb temperature values. (Details of the procedures of sampling and data reduction are given in the Appendix.)

The average amount of heating required was calculated (see Appendix for method) for that fraction of operating time during which the wet-bulb depression was less than the chosen value.

The results of the analysis are given in Table II. It is assumed that costs of steam and electricity are as quoted earlier and that air heating is by means of steam pipes.

Comparing the figures in the last column with that previously calculated for the operation of an

efficient steam-heated dryer, i.e., .43d./lb., it appears that when climatic conditions are taken into account the unheated-air dryer has a slight advantage in relatively dry locations; elsewhere the costs are slightly in favor of steam heating. However certain advantages already mentioned which accrue from the use of unheated air may render it on balance the more attractive alternative.

An estimate of the performance of an unheated-air dryer at any proposed location may be gained by comparing the relevant climatic data with those quoted in Table I. When required, a fuller analysis may be made by the method described in the Appendix.

### Air Flow in a Dryer Using Unheated Air

As pointed out earlier, if wool is to be dried uniformly to a particular value of regain then the water-removing capacity of the drying air depends very little on its initial temperature (Figure 1). The air-blowing energy required per pound of water removed is therefore comparable in value for an unheated-air dryer and a steam-heated dryer. An essential difference between the designs, however, is that in the unheated-air dryer, air, having passed through the wool once and become saturated, is then exhausted, while in a steam-heated dryer the air is heated so as to be below saturation point and then passed through the wool again, this process usually being repeated many times (recirculation). Consequently the air intake rate is far higher in an unheated-air machine. To illustrate, an unheated-air dryer removing 1.0 g. of water per cubic meter of ingoing air (under standard atmospheric conditions) may be compared with a steam-heated dryer exhausting at 180° F., 50% RH, and carrying away 165 g./m.$^3$ The required rate of air intake in the former case is therefore 165 times as great as for a steam dryer of the same drying performance.

Non-uniformity of packing of the wool layer is undesirable both in conventional dryers and in dryers of the present design, particularly if it is so pronounced that gaps exist in the layer through which air can flow freely. In conventional dryers non-uniform packing can produce uneven drying or overdrying and increase the amount of recirculation required and the drying time. In an unheated-air dryer it cannot cause overdrying but will necessitate increased air consumption and hence lower the efficiency; a practical dryer design should therefore include means for producing a reasonably uniform layer of wool.

The amount of solid matter filtered from the air by unit mass of wool during the large air flow required is negligibly small. Even under the most severe conditions of atmospheric pollution (1 mg./m.$^3$), the amount filtered as a fraction of the mass of wool dried is 0.5 parts per 1000. Air filtering may not be needed.

For the case, studied earlier in the paper, of an unheated-air dryer producing 800 lb. of wool per hour, the pressure drop across the wool layer can be found, using Equation 1 and values previously given for the parameters, to be 5.2 cm. (2 in.) of water; this is a normal figure in dryer design.

In the unheated-air dryer proposed here, the relative humidity of the air passing through the wool can be directly controlled, and since the wool is brought to equilibrium with the drying air, the regain of the outgoing wool may therefore also be directly controlled. On the other hand, in steam-heated dryers of conventional design with recirculated air, the relative humidity can only be controlled by temperature adjustments in the various stages and is subject to variations arising from changes in the rate of water removal and hence in the packing and thickness of the wool layer, its water content, etc. Control of regain is therefore more difficult in these machines.

The danger of overdrying or damaging the wool should be much lower in an unheated-air dryer than in the steam-heated type, where misadjustment of

**TABLE III. Tests of Pilot-Scale Unheated-Air Dryer**

| | Test No. 1 | Test No. 2 |
|---|---|---|
| Average wet-bulb depression, deg. C. | 3.5 | 3.6 |
| Output of dryer, lb./hr. | 21 | 24 |
| Initial regain, % | 73 | 72 |
| Final regain, % | 21 | 22.5 |
| Air flow, m.$^3$/min. | 96 | 93.5 |
| Drum speed, revs./hr. | 5.3 | 6.0 |
| Pressure drop across bed, cm. water gauge | 6.3 | 5.0 |
| Average rate of removal of water, g./m.$^3$ of air | 0.71 | 0.80 |
| Equivalent rate of removal of water at depression of 4.2° C., g./m.$^3$ | 0.85 | 0.96 |

temperature or low moisture content in the recirculating air can lead to low values of regain.

A simple method of determining the atmospheric wet-bulb depression is available in the unheated-air dryer: the temperature drop across the wool may be measured at an early stage of the drying process, when the outgoing air is saturated; this measurement may be used to control, manually or automatically, the humidity of the ingoing air. Furthermore, at the end of the drying process the temperature depression across the wool will be approaching zero, and a measurement of the depression at the output of the machine thus provides a check on whether the required drying rate is being achieved.

The large amount of low-temperature, saturated air exhausted from the dryer may be used to advantage in plants where air humidification is required for subsequent textile operations.

Summarizing, we may list as follows the features of a dryer based on the use of unheated air: (i) savings in operating costs over those of an efficient steam-heated dryer of conventional type; (ii) good control and uniformity of regain of the dried wool; (iii) danger of overdrying reduced; (iv) size and mechanical complexity comparable with conventional dryers, but need for insulation eliminated; and (v) moist output air available for mill conditioning.

## Pilot-Scale Dryer

It is recognized that considerable difficulty may arise in practice in the design and construction of a large-scale drying machine embodying the principles discussed here. For example there may be difficulty in handling the large volumes of air required to be taken in and exhausted by the machine, or in forming a sufficiently uniform layer of wool to ensure that the efficiency of water pick-up is not seriously impaired. To investigate some of the possible difficulties a pilot-scale dryer based on the use of unheated air was built, using the suction drum principle. A single cylinder, 2 ft. in diameter and 1 ft. 10½ in. wide, has its peripheral surface perforated with 0.3-in. holes at ½-in. centers and can be rotated via a belt drive at any required speed. Air from the room is sucked through an axial duct, using a straight-blade centrifugal fan driven by a 5-h.p. motor. A feed belt delivers wool direct to the drum at any required rate, where it is held by suction. After rotation through 290° the wool drops off into a bin, the air flow through the drum being blocked at this point by an internal baffle.

With this simple arrangement it is not possible to control the humidity of the ingoing air. The dryer has therefore been evaluated by making a number of tests over a range of values of atmospheric wet-bulb depression.

To illustrate the performance, results are tabulated in Table III for two tests made on days of low depression, which is an unfavorable situation.

The tests on the stationary bed gave a figure of 1.1 g./m.³ for a depression of 5.0° C. This is equivalent to 0.9 g./m.³ for the standard depression of 4.2° C. The results from the pilot-scale dryer confirm this result and point to the practicability of large-scale dryers using unheated air.

## Literature Cited

1. Baxter, S. and Cassie, A. B. D., *Trans. Faraday Soc.* **37**, 506 (1941).
2. Cassie, A. B. D., *Trans. Faraday Soc.* **36**, 453 (1940).
3. Cassie, A. B. D. and Baxter, S., *Trans. Faraday Soc.* **36**, 458 (1940).
4. Daniels, H. E., *Trans. Faraday Soc.* **37**, 506 (1941).
5. Downes, J. G., Australian Patent Application 30889/57.
6. Downes, J. G. and McMahon, G. B., TEXTILE RESEARCH JOURNAL **29**, 1006–1010 (1959).
7. King, G. and Cassie, A. B. D., *Trans. Faraday Soc.* **36**, 445 (1940).
8. McMahon, G. B. and Downes, J. G., "Propagation of Temperature and Moisture Changes During Forced Convective Flow of Air through a Mass of Hygroscopic Fibres," submitted to *Intern. J. Heat Mass Transfer.*
9. Wool Industries Research Association, "Wool Research," Vol. 2, "Physical Properties of Wool Fibres and Fabrics," Chapter 2, Leeds, W.I.R.A., 1955.

*Manuscript received November 23, 1959.*

## Appendix: Analysis of Meteorological Data to Assess Dryer Performance

The meteorological data used were in the form of tabulated values of dry- and wet-bulb temperature recorded at hourly or 3-hourly (9 a.m., 12 noon, etc.) intervals. Only the values corresponding to the hours of a normal working day were considered. The data used covered a continuous period of 5 years (1953–57). The total number of pairs of values available from each location was about 20,000 (from hourly records) or 5,500 (from 3-hourly rec-

ords). In each case a sample of about 600 pairs was chosen. Stratified sampling was adopted to ensure correct representation from the sub-groups, i.e., each hour of the day and month of the year. Sampling was on the basis of random selection of days in the month, using tables of random numbers.

The fraction of operating time for which the wet-bulb depression was less than 8° F. (i.e., time during which air heating was required) was found directly from the sample. To find the amount of heat required in such cases it is necessary to determine the amount by which the dry-bulb temperature must be raised so that the depression becomes 8° F. The relevant formula is (assuming constant water vapor pressure)

$$\Delta T_d = \left(1 - \frac{\tan \beta}{\tan \alpha}\right) \Delta T_w \qquad (1)$$

where $\Delta T_d$ = necessary increase in dry-bulb temperature $T_d$, $\Delta T_w$ = difference between actual wet-bulb depression and 8° F., $\tan\beta$ = slope of the "line of adiabatic saturation" or "wet-bulb line" on a plot of water vapor pressure vs. air temperature [6, 9], $\tan\alpha$ = slope of the "saturation" curve on the aforementioned plot. Formula 1 is strictly true only for very small values of $\Delta T_d$ and $\Delta T_w$, and $\tan\alpha$ is then evaluated for the appropriate value of $T_d$. In practice $\Delta T_d$ and $\Delta T_w$ may have values of some degrees, and an average value of $\tan\alpha$ should be taken. A convenient method we have adopted, which is sufficiently accurate for the range of values involved, is to evaluate $\tan\alpha$ in each case at a temperature $(T_d - 3)$° F. As an example, assume that at a particular hour the dry- and wet-bulb temperatures were 70° and 65° F., respectively. Then

$$\text{Wet-bulb depression} = 5° \text{ F.}$$
$$\Delta T_w = 3° \text{ F.}$$
$$\tan \beta = -.36 \text{ mb/°F.}$$
$$\tan \alpha \text{ (evaluated at 67° F.)} = .78 \text{ mb/°F.}$$

whence

$$\Delta T_d = 1.46\, \Delta T_w = 4.4° \text{ F.}$$

To find the amount of heat required per pound of water removed we assume, as in the paper, that the air removes 46% of the theoretical amount, i.e., 1.1 g./m.$^3$ or $6.86 \times 10^{-5}$ lb./ft.$^3$. The heat capacity of air at room temperature is $1.795 \times 10^{-2}$ B.T.U./°F./ft.$^3$, so that the heat required to raise it 4.4° F. is $7.89 \times 10^{-2}$ B.T.U./ft.$^3$. Hence the heat required per pound of water removed is

$$\frac{7.89 \times 10^{-2}}{6.86 \times 10^{-5}} = 1150 \text{ B.T.U./lb.}$$

At the previously assumed steam cost of $2.4 \times 10$d./B.T.U. the cost of heating is 0.28d. per pound of water removed.

# Moduli of Cotton Fibers and Yarns in Relation to X-Ray Angles

**Louis C. Weiss, Rollin S. Orr, Jerome J. Redmann,[1] and James N. Grant**

*Southern Regional Research Laboratory,[2] New Orleans, Louisiana*

**Abstract**

Cotton samples with a wide range in fiber properties were chosen. An X-ray measure of the degree of crystallite orientation and/or the secant modulus of fifteen cottons are traced through levels from sub-fibers to single fibers to bundles to yarns. The differences due to sample characteristics gradually become less as the cottons progress through these levels. When the secant modulus of the yarns spun at the appropriate twist for maximum strength is referred to the X-ray measurement, no additional masking, but resolution occurs. The resolution seems to be more pronounced with American upland than with *barbadense* cottons. Tenacity, secant modulus, and bundle linear density primarily explain the rankings.

## Introduction

Differences in certain properties of cotton fibers produce observable differences in properties of the yarns made from them. However, processing parameters often overshadow possible causal differences in the fibers. The lack of knowledge regarding the role of single fibers in fiber processing and in yarn properties has been due in no small part to the extremely complex structures of cotton fibers and yarns. In recent years several relationships between fiber tensile properties and cellulosic structural variables have been analyzed [6, 9]. Rebenfeld and Virgin have shown a relationship between X-ray angle and single-fiber "elastic" modulus [11]. Fiori et al. have correlated the secant modulus of fiber bundles with that of cotton yarns [4]. Progress is being achieved in characterizing cotton fibers and fiber products according to a stress–strain modulus of the material.

In the present investigation of fiber and yarn properties, attempts have been made to use X-ray angle and secant modulus to trace the behavior of different cotton varieties from below the fiber level through the single-fiber and fiber-bundle levels to the yarn level. The information obtained from these indices of the stress–strain modulus is used to indicate how fiber properties are retained or transformed in the final yarn structure.

## Experimentation

### *Samples*

The samples represented cottons from both commercial and experimental varieties. The X-ray angle, bundle tenacity, and bundle elongation at break were measured on specimens from the card sliver of 43 different samples. From these samples, fifteen cottons were selected for single-fiber tensile evaluation. Single fibers were chosen at random from a homogenized sample composed of the fibers of the modal length and the two adjacent length groups of a fiber length distribution. Both fiber and bundle groups included cottons with wide ranges in their physical properties. Conventional fiber measurements such as length, maturity, and Micronaire fineness of the ginned cottons as well as the tensile properties of 40 (15/1) and 20 (30/1) tex yarns were available from another investigation [4].

### *Tests*

Variables in testing such as the length of the specimen under strain and the method used to measure the properties should be considered in any final conclusions based on load and elongation values. Yet, for the purpose of tracing a modulus through the several different experimental levels from subfiber through yarn, the following standard tests were utilized.

[1] Resigned.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

The index of crystallite orientation (X-ray angle) was measured in duplicate from bundles of parallel fibers using a recording X-ray spectrometer [3, 12]. The X-ray angle measured was one-half of the angular width of the peak in degrees at 50% of the maximum intensity of the diffraction arc from, essentially, the 002 crystallite plane. The single-fiber tensile properties were measured with the TRI-Schaevitz tester [3] with the crosshead speed set at 0.04 mm./sec. The load–elongation curves were determined for 100 single fibers mounted at a gauge length averaging about 8.4 mm. The measurements of gauge length for ten fibers from each of the samples gave a range of 8.1–8.9 mm. when the individual fibers were under a 0.1-g. load. The linear density (weight fineness) for a group of 100 fibers was measured prior to loading for each of the fifteen cotton samples.

The bundle load and elongation at break were measured with the Stelometer [3] on seven specimens of each sample with clamp spacings of both zero and 3.2 mm. by each of three operators [15]. The rate of loading was set at 1.0 kg./sec. Specimen size was controlled to provide average breaking loads of about 5.0 kg. [10].

Yarn load and elongation at break had been measured with the Uster single strand tester [3] at a gauge length of 50 cm. Length, Micronaire fineness, and maturity measurements were determined according to A.S.T.M. methods [1]. All tests except the X-ray angle measurements were made under atmospheric conditions controlled at 70° F. and 65% RH.

## Results and Discussion

### *Characteristics*

The curves in Figure 1 illustrate the range in the stress–strain properties of single fibers found for the 15 cottons. The curve for each cotton is an average of curves from ten fibers whose breaking loads and elongations match as closely as possible the means for the 100 fibers. The ten elongations are averaged at five equal load spacings and the tenacity is calculated from the load and from the linear density of 100 fibers. Other mechanical properties which can be derived from the stress–strain curve are used to relate X-ray angle to fiber and yarn properties. The area under a curve (approximated by one-half the product of the end points of tenacity and percent elongation) denotes the toughness, or energy-absorbing capacity, of a fiber. The general slope (derived from the zero-to-end point values of tenacity divided by per cent elongation) denotes the secant modulus, also referred to as average stiffness, of the fiber.

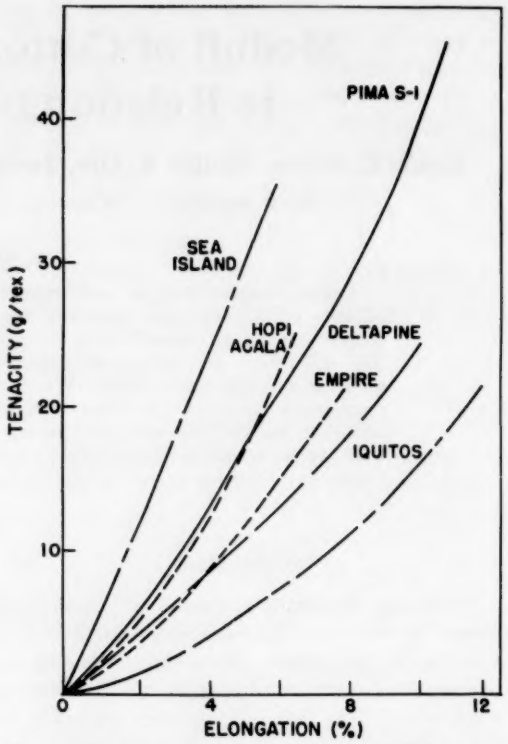



**Fig. 1.** The tenacity–percent elongation curves for single fibers of six cottons differing widely in physical properties.

Measurements on the 43 cottons from which the selections for the investigation of single fibers were made showed relationships between structural and physical properties of the fibers. A decrease in strength with increase in gauge length exists for both single fibers and fiber bundles. The decrease in strength may be expressed as the difference, the per cent difference, or the ratio of tenacities as measured at two different clamp spacings [5, 6, 10]. The change, an index or estimate of the uniformity of tenacity along the specimen length, is attributed to weak points existing along the fiber. The X-ray

[3] Trade names are used to facilitate identification. The Department does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

angle is presently utilized as an index of the average angular orientation of the crystallites in the spiraling fibrillar structure of the cotton fiber. The X-ray angle has been related to the strength of bundles at zero clamp spacing and to the uniformity of strength along the length of the fiber [6, 9, 11]. For the 43 cottons, the correlation is improved by extrapolating bundle-tenacity–gauge-length curves to a value of approximately 0.1 mm. The corresponding tenacity value has a linear correlation coefficient of $-0.85$ with the X-ray angle. The regression equation is $T = -2.1X + 107.8$ with a standard error of 3 where $T$ is the extrapolated bundle tenacity in g./tex and $X$ is the X-ray angle in degrees. Since weak points and spiral structure affect strength, it is logical that the extrapolated bundle tenacities at the short gauge length correlate better with the X-ray angles than the measured tenacities at either zero or 3.2-mm. clamp spacing.

The bundle secant modulus for each of the 43 cottons was calculated from measurements of tenacity and elongation per unit length determined at 3.2-mm. spacing. The correlation coefficient of this modulus with the X-ray angle is $-0.80$. The regression equation is $M = -27X + 984$ with a standard error of 42 where $M$ is the secant modulus in g./tex and $X$ is the X-ray angle in degrees. The high correlation is encouraging considering the uncertainties in the measurements of both spiral angle and secant modulus for fiber aggregates [8, 15].

*Secant Modulus*

A method of using single-fiber tenacity and per cent elongation to calculate these same properties for bundles has been reported [10]. And, as the secant modulus of bundles has been shown to be important in yarn properties [4], it is reasonable that this modulus of single fibers should be basically related to the same modulus in yarns. Table I presents the secant modulus of single fibers, fiber bundles, and yarns in addition to values for the conventional properties of the fifteen selected samples. These cottons are listed in order of increasing secant modulus in the fibers; there are only limited shifts in the ranking according to this modulus at the bundle and yarn levels. Significant exceptions are the unusual changes in the secant moduli of Tanguis and Karnak from single fibers to bundles. These shifts are in the direction which could be partially explained by the low coefficients of friction reported for these two varieties [7]. As these two cottons have among the highest coefficients of variation in both breaking tenacity and per cent elongation, part of the decreases could be due to combinations of statistical variations and experimental errors occurring in the determination of the fiber properties.

**TABLE I. Physical Properties of the Fifteen Cottons Selected for Single-Fiber Evaluation**

| Samples* | Suter-Webb UQ length, in. | Micronaire reading | NaOH maturity, % | X-ray angle,‡ degree | Tenacity, g./tex | | Secant modulus, g./tex | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | Yarn | |
| | | | | | Single fiber | Fiber bundle** | Single fiber | Fiber bundle** | 15/1 | 30/1 |
| Iquitos | 1.11 | 7.1 | 96 | 30.8 | 21.0 | 17.4 | 170 | 170 | 156 | 142 |
| American† | 0.99 | 5.0 | 80 | 27.9 | 22.2 | 15.2 | 230 | 220 | 191 | 179 |
| Rowden | 1.10 | 5.7 | 92 | 27.5 | 22.5 | 18.2 | 230 | 220 | 200 | 179 |
| Deltapine 15 (I) | 1.24 | 4.6 | 92 | 30.0 | 24.7 | 19.4 | 240 | 200 | 198 | 210 |
| Empire | 1.12 | 3.9 | 76 | 28.8 | 20.2 | 16.8 | 250 | 230 | 160 | 190 |
| Deltapine 15 (II) | 1.22 | 4.4 | 90 | 27.4 | 26.4 | 19.5 | 280 | 240 | 198 | 199 |
| Acala 4-42 | 1.21 | 3.5 | 80 | 28.6 | 22.0 | 17.3 | 290 | 250 | 220 | 207 |
| Tanguis | 1.31 | 4.7 | 89 | 31.1 | 30.5 | 18.3 | 310 | 180 | 184 | 179 |
| Wilds | 1.42 | 3.9 | 92 | 27.8 | 28.1 | 21.3 | 330 | 280 | 226 | 236 |
| Interspecies | 1.06 | 3.6 | 86 | 23.3 | 28.2 | 21.9 | 380 | 350 | 298 | 264 |
| Pima S-1 | 1.42 | 3.9 | 94 | 28.6 | 44.7 | 28.4 | 410 | 290 | 277 | 292 |
| Hopi Acala 50 | 1.09 | 4.6 | 96 | 24.4 | 25.8 | 21.7 | 430 | 350 | 295 | 264 |
| Hopi Acala 54 | 1.19 | 4.7 | 90 | 24.0 | 28.6 | 22.6 | 430 | 370 | 299 | 264 |
| Karnak | 1.42 | 3.2 | 86 | 28.9 | 39.2 | 24.0 | 460 | 300 | 249 | 245 |
| Sea Island | 1.95 | 2.7 | 80 | 24.4 | 35.6 | 29.0 | 570 | 460 | 358 | 358 |

* In order of increasing secant moduli of single fibers.
† Unknown variety of upland commercial cotton.
‡ 50% of maximum intensity.
** 3.2 mm. clamp spacing.

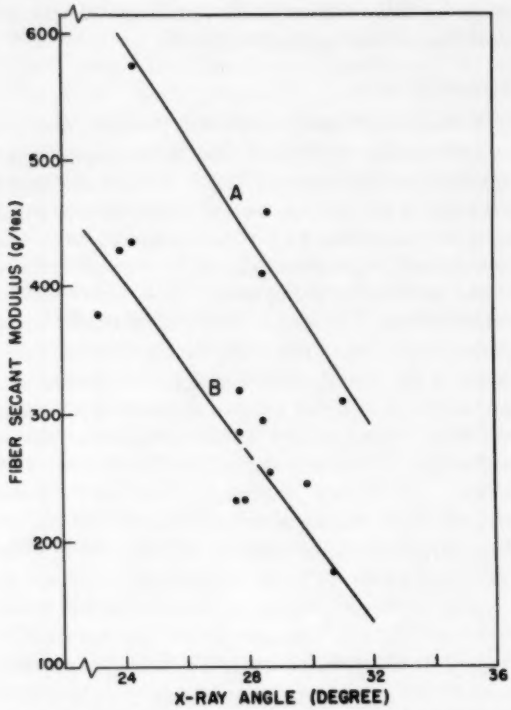



**Fig. 2.** The secant modulus of single fibers as a function of X-ray angle. A, *barbadense;* B, essentially *hirsutum* type cottons.

*Single Fibers*

When the secant modulus of the single fibers is compared to the more fundamental X-ray angle measurement, a series of useful connecting transformations becomes apparent. The X-ray angle has been shown to be related to bundle secant modulus as well as to tenacity. Furthermore, the X-ray angle indicates a maximum possible per cent elongation [9]. For the fifteen cottons measured, single-fiber per cent elongation is, within the correct order of magnitude, a function of the X-ray angle and the number of reversals in spiral structure of the fibers. These results are not in conflict with the postulation that the X-ray angle is a possible indicator of the features determining a longitudinal "elastic" modulus of cotton below the fiber level, i.e., a sub-fiber "modulus." (Improved techniques and analyses of single-fiber and X-ray measurements should yield additional knowledge of an inverse relationship between true helix angle and fiber modulus.)

Figure 2 shows that a fiber structure parameter, the X-ray angle, is associated with the secant modulus of the single fibers for a wide range of cottons. There is seemingly a family of relationships. Line A is composed of four cottons whose fibers have unusually high tenacities. Three of these cottons, Sea Island, Karnak, and Pima S-1, are of the *G. barbadense* type. The other cotton, Tanguis, is sometimes classified with this type. Line B is formed from the rest of the cottons listed in Table I.

*Fiber Bundles*

In Figure 3 a direct correspondence is shown when relating the secant moduli, in these fifteen cottons, of the single fibers to those of the bundles, tested with about 8.4 and 3.2 mm. initial jaw separation, respectively. In the graph the separation according to genetic type is still apparent; but interaction among the fibers in aggregates is beginning to mask the differences among samples so that there is less differentiation between the two types of cotton.

*Yarns*

The data of Table I show that the secant moduli of the yarns rank in nearly the same order as the moduli of the bundles. This relationship is in agreement with similar results for the 43 cottons [4]. However, the two types of cotton now lose their identity. In the linear relationship of yarn secant modulus to bundle secant modulus, the change for yarns is approximately 0.7 times the corresponding change for the bundles.

Going from the secant modulus of single fibers to that of yarns in one step, the change of modulus for the yarns is approximately 0.4 times the corre-

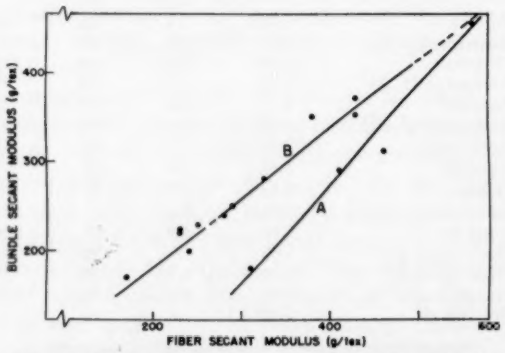



**Fig. 3.** The secant modulus of fiber bundles as a function of the secant modulus of single fibers. A, *barbadense;* B, essentially *hirsutum* type cottons.

sponding change for single fibers. Also, the two types of cotton combine, as before, into one relationship. The sample differences of single fibers are considerably masked by the process of yarn construction. This emphasizes a difficulty in using a limited number of fiber properties which vary with variety as guides for improving cotton breeding, processing, and utilization.

*Sub-Fiber to Yarns*

If the secant modulus of the yarns is plotted against the X-ray angle, further spreading than occurred with fibers and bundles (Figures 2 and 3) is observed. The spreading can be interpreted as diffraction, or separating into sub-groups, according to other fiber differences. The results for these fifteen cottons are presented in Figure 4. The dashed-line, A, represents those cottons of the highest tenacities, i.e., Sea Island, Pima S-1, and Karnak. The solid-line, A′, includes these cottons plus Tanguis, which is located near the intersection of lines A′ and B. The lowest curve, B′, is composed of Iquitos, Empire, Rowden, Deltapine 15 (II), and the unknown American upland cotton. The remaining cottons of Table I compose the middle curve, B.

No preference is implied for either the A or A′ curve. But, with reference to X-ray angle and either of these curves, the yarns of Pima S-1 have a high secant modulus of 285 g./tex. The ability of Pima to achieve high strength transfer is in agreement with the good characteristics of the yarns made from this cotton [2]. These characteristics may conceivably be due to the high toughness of the Pima fiber at a moderate secant modulus (see Figure 1). In contrast, the cumulative inability of Tanguis to transfer single-fiber strength properties to yarns may be a reason for its downward shift onto the general curve of upland cottons. Processing seemingly resolves these cottons into three groups according to basic fiber differences. The five cottons of B′ also fall below the single-dash break shown on the B curves in Figures 2 and 3, indicating that the difference common to these five cottons was present but was not obvious in the preceding comparisons.

If a fiber property (or combination of properties) of the cottons represented in the B and B′ curves is more sensitive to mechanical processing than the same property in the other cottons, a measurement of its value should explain the secondary separation. A knowledge of this property would be of assistance in using fiber properties for predicting processing ability, yarn structure improvements, and specialized product utilization. The separation into the two lower curves is considered important, as these cottons are mostly American upland commercial types.

*Behavior of Cottons*

Although single-fiber tenacity helps to explain the curves obtained at each level of measurement, it does not completely explain the difference between the cottons represented by the curves B and B′. Since stress–strain moduli have been useful in examining the stepwise transition from sub-fiber to yarn, it is logical that the secant modulus of single fibers should be investigated as an index of the over-all transition covering the same levels. The solid-line, A′, would be the top curve in Figure 4 if the pre-

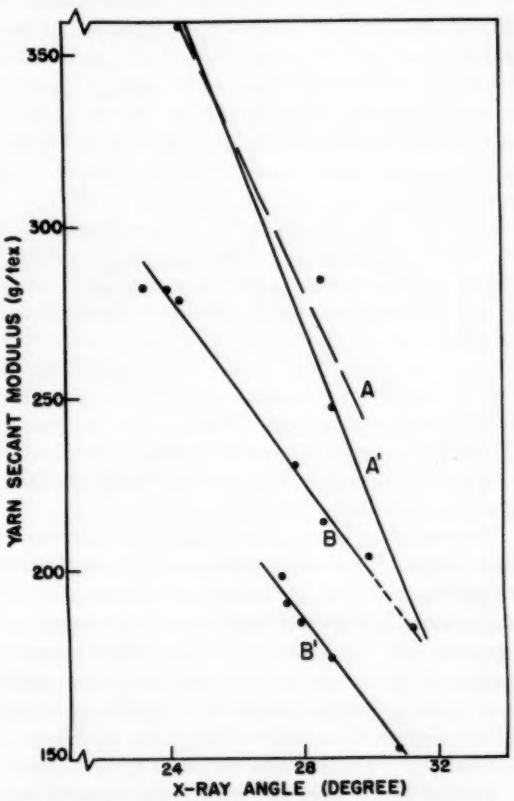



**Fig. 4.** The average secant modulus from 15/1 and 30/1 (40 and 20 tex) yarns as a function of the X-ray angle. A and A′, *bardadense;* B and B′, essentially *hirsutum* type cottons.

diction were based only upon the single fibers. If the prediction were based upon bundles, the top curve in Figure 4 would be the dashed-line, A. The secant modulus of bundles aids in the interpretation of this shift because of the behavior of fiber aggregates of Tanguis (see Table I). Hence, the secant modulus of single fibers is transferred to bundles and again to yarns. Finally optimum presentation is obtained when the secant moduli are plotted as functions of the X-ray angles (Figures 2 and 4). Unfortunately X-ray angle alone may yield a double-valued prediction of secant modulus. Another property, less likely to be a pre-eminent function of secant modulus or X-ray angle, would be more meaningful as far as mill processing is concerned and would be of additional assistance in understanding yarn structure. Bundle linear density (center weight fineness) in conjunction with tenacity explains the resolution of all curves without conflicts. Measurements of several other properties give many conflicts. Fiber, bundle, and yarn tenacities individually or in combinations with each other yield limited conflicts usually involving Deltapine 15 (1) or Acala 4-42. A combination of tenacities advantageous in explaining the resolution of curves B and B′ is found in an approximation for the quantity[4] $F_a/\lambda$ [13]. A measure of such a ratio can be approximated either by dividing the theoretical strength of an idealized roving by the tenacity of its component single fibers or by obtaining the tenacity ratio after extrapolating to obtain the bundle tenacity at a gauge comparable to that in single-fiber tests. The uniformity of bundle tenacity with gauge length was the next most useful strength parameter. These ratios of efficiency of tenacity transfer and of the tenacity–length uniformity are discussed in detail in a study of cotton fibers in yarn structure [14].

The variables involved in going from sub-fiber to yarn suggest that basic differences in single-fiber properties must be overcome to achieve ultimate utilization of the fiber in the yarn. In an attempt at compensation, increased twist multipliers are required to secure maximum strength in the yarns from those cottons that form the B′ curve. Cottons on this line are observed to have lower efficiency in transferring per cent elongation from fibers to yarns.

Further investigations of such variables as elongation of fibers within the yarns and "elastic" modulus on the complete stress–strain curve are needed. Additional information on fibril spiral angle and such constants of cotton fibers as friction and convolutions would contribute to the analysis of fiber–yarn relationships.

[4] The *efficiency of tenacity transfer* is suggested as a convenient and descriptive name for this ratio.

## Summary

The observation that differential fiber behavior gradually diminishes from the sub-fiber level through to the yarn level is useful for unifying fiber investigations. The step-by-step investigation is also helpful in analyzing the single encompassing step which showed spreading when going from X-ray angle measurement to yarn secant modulus. The resolution of representative American upland cottons into two sub-groups and their possible definition in terms of analytical theory or empirical hypothesis are considered to be useful in programs of cotton fiber modification, processing, and breeding. The anomalous behavior observed in going from single fibers to bundles in such cottons as Tanguis was partially explained. No single property of the fibers exactly satisfies the demanding test of individual ranking for these fifteen cottons.

This analysis illustrated the importance of the measurement of X-ray angle and fiber modulus in predicting behavior of fibers in cotton yarns. Clues were obtained as to the possible role, in theories of cotton yarn structure, of the stress–strain modulus, the bundle linear density, the uniformity of tenacity with gauge length, and the efficiency of tenacity transfer from single fibers to idealized rovings.

## Acknowledgments

The authors wish to express their appreciation to Ruby H. Tsoi and Emilie H. Nott for statistical assistance, to Malcolm E. Whatley for assistance in X-ray angle measurements, to Louis A. Fiori and Annie B. Cooper for making available details on the conventional properties of the yarns and ginned cottons used, and to George I. Pittman for the drawings.

## Literature Cited

1. American Society for Testing Materials, Committee D-13, "ASTM Standards on Textile Materials (with Related Information)," Philadelphia, 1956.
2. Brown, J. J., Howell, N. A., Fiori, L. A., and Sands, J. E., TEXTILE RESEARCH JOURNAL **25**, 404–414 (1955).
3. Creely, J. J., Segal, L., and Ziifle, H. M., TEXTILE RESEARCH JOURNAL **26**, 789–795 (1955).

4. Fiori, L. A., Sands, J. E., Little, H. W., and Grant, J. N., TEXTILE RESEARCH JOURNAL **26**, 553–564 (1956).
5. Grant, J. N. and Morlier, O. W., TEXTILE RESEARCH JOURNAL **18**, 481–487 (1948).
6. Hertel, K. L. and Craven, C. J., TEXTILE RESEARCH JOURNAL **26**, 479–484 (1956).
7. Lord, E., *J. Textile Inst.* **46**, T191–213 (1955).
8. Meredith, R., *J. Textile Inst.* **37**, T205–218 (1946).
9. Orr, R. S., DeLuca, L. B., Burgis, A. W., and Grant, J. N., TEXTILE RESEARCH JOURNAL **29**, 144–150 (1959).
10. Orr, R. S., Weiss, L. C., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 939–946 (1955).
11. Rebenfeld, L. and Virgin, W. P., TEXTILE RESEARCH JOURNAL **27**, 286–289 (1957).
12. Segal, L., Creely, J. J., and Conrad, C. M., *Rev. Sci. Instr.* **21**, 431–435 (1950).
13. Sullivan, R. R., *J. Appl. Phys.* **13**, 157–167 (1942).
14. Weiss, L. C., Tsoi, R. H., Sands, J. E., and Grant, J. N., "Effect of Cotton Fiber Tenacity Ratios on Optimum Yarn Twist," in preparation for publication.
15. Weiss, L. C., Orr, R. S., Nott, E. H., and Grant, J. N., "Reliability in Cotton Bundle Testing," in preparation for publication.

*Manuscript received July 25, 1960.*

# Kinetic Studies of the Wool-Water System

## Part III: The Mechanism of Sorption at High Water Concentrations

**I. C. Watt and J. E. Algie**

*C.S.I.R.O. Wool Research Laboratories, Division of Textile Physics, Ryde, N.S.W., Australia*

**Abstract**

Kinetic studies of the sorption of water, following a change of water vapor pressure surrounding wool fibers and horsehair with a high initial or final water content, are described. The processes of absorption and desorption show non-Fickian behavior over the entire course of water content change. An additional non-Fickian anomaly, present for both integral and interval absorption, is an overshoot above the final equilibrium concentration of water in the fibers. It is apparent that the initial molecular configuration of the keratin has a marked influence on the sorption behavior. The effect is greater at the high relative humidities of the experiments reported in this paper than at intermediate relative humidities (approximately 50% RH) as reported in Part II.

Data obtained by a vibroscope technique show a different course of absorption, for the same changes of relative humidity around the fiber, than is found for the samples on the sorption balance. The non-Fickian nature of the process is evident in both techniques.

PART I [10] of this series described the sorption behavior of the wool–water system following large-step (integral) and small-step (interval) changes of water vapor concentration at the surface of the fibers. The form of the sorption curves varied markedly with the initial water concentration in the fibers. For absorption to water concentrations of 0–2.5% the uptake followed Fick's laws of diffusion. The corresponding desorption also was Fickian initially but showed a long-term slow approach to dryness. Integral absorption and desorption to and from water concentrations above 2.5% in the wool fibers showed increasing deviation from Fick's laws of diffusion as the equilibrium water concentration increased. Interval absorption into fibers already containing more than 2.5% of water showed a distinct two-stage character until the initial equilibrium water content was higher than 19%.

For both integral and interval absorption to high water concentrations the phenomenon of a concentration overshoot was observed, i.e., the total amount of water within the fibers passed through a maximum before settling to the equilibrium value for the particular vapor pressure outside the fibers.

In Part II [11] the sorption behavior in the range of intermediate water concentrations within wool fibers was examined in more detail and the probable mechanisms of the two-stage interval absorption were discussed. It was shown that as the initial water concentration increased the two stages of absorption tended to merge to form an uptake curve where it was no longer possible to separate the kinetic behavior into two distinct stages. In the final paper of this series we wish to present more data on the sorption behavior for keratin fibers with a high initial or final water content and to discuss the complex nature of both absorption to, and desorption from, high water concentrations within the fibers.

## Experimental Method

The apparatus, experimental technique, and preparation of the samples for the sorption experiments using a McBain-Bakr sorption balance, have been fully described [10]. Some comparative experiments were performed using a vibroscope technique in which the fiber was suspended in the same apparatus from a fixed support, between a pair of condenser plates which were charged to cause the fiber to vibrate. A mass was attached to the end of the fiber to provide a tension. The phototransistor which detected the vibration was mounted outside the glass walls of the sorption chamber. The use of a vibroscope technique for kinetic sorption studies of wool fibers has been reported by Downes and Mackay [2].

## Results

### *Absorption Overshoots*

*Integral absorption.* An overshoot above the equilibrium water concentration was observed for large water vapor pressure increments to high relative humidities. Figure 1 shows the integral absorption curves for Corriedale wool at three temperatures, for a relative humidity step of approximately 0–95%. It is apparent that the size of the uptake overshoot increases with increasing temperature, while the time to attain final equilibrium becomes less. Although the initial rate of uptake is increased, the equilibrium water concentration decreases with increasing temperature, as has been reported by a number of workers. Despite the fact that the size of the uptake overshoot is greater at higher temperatures, the maximum water content reached also decreases with increasing temperature.

*Interval absorption.* It was shown in Part I that the uptake curve, following a small vapor pressure increment applied to wool with a high initial water concentration, showed an inflection as a function of $(\text{time})^{\frac{1}{2}}$ and passed through a maximum before settling to the final equilibrium value of water concentration. This behavior was observed for a sample of wool fibers which had been taken from dryness in a series of interval steps. If the water content of the fibers had been increased rapidly to a high value and then subjected to a series of small vapor pressure increments, the initial water concentration from which absorption overshoots were first observed was higher. It has been shown by Watt and Kennett [13] that the molecular configuration of wool fibers undergoes a change when the wool is equilibrated with water vapor at intermediate relative humidities. When the wool was subsequently taken to a high relative humidity the changes of molecular configuration were not reversed unless the fibers were saturated. Thus wool taken to a high humidity by a series of small steps, with equilibrium water content allowed to be established after each such step, is in equilibrium with water vapor at intermediate relative humidities for a period of weeks. This is sufficient time to cause a marked difference in molecular configuration relative to that of wool taken to a high relative humidity in one step.

It was reported in Part I that, for a series of interval absorption steps, absorption overshoots occurred for any steps in which the wool was initially equilibrated with water vapor above 80% RH and two-stage absorption behavior was no longer evident. It has been found that, if the interval absorption followed an integral absorption step, it was necessary

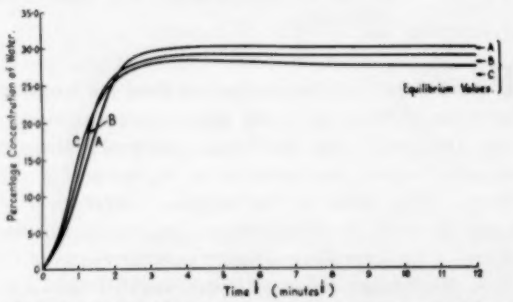



**Fig. 1.** Integral absorption at three temperatures. Water uptake vs. $(\text{time})^{\frac{1}{2}}$ following: Curve A, a 0–94.4% relative humidity step at 20° C; Curve B, a 0–94.9% relative humidity step at 35° C; Curve C, a 0–95.1% relative humidity step at 50° C.

for the integral absorption step to be one to 85% RH before the subsequent interval step lost its two-stage absorption character and an absorption overshoot was observed. It appears therefore that the molecular configuration of the wool fibers, as well as the initial water concentration of the fibers, influences the observed sorption behavior.

When absorption overshoots are observed, the form of the uptake curve is similar irrespective of the size of the concentration increment, i.e., no two-stage uptake is observed as at intermediate vapor pressures. There is, however, a method of varying the uptake curve which throws some light on the mechanism of absorption operative for fibers with a high water content. That is to alter the elapsed time between the commencement of one absorption step and the beginning of a second step. In Part I a typical uptake curve between the limits of 79.4% and 94.8% RH was shown. The maximum water content of 30.6% was reached 20 min. after the increase of vapor pressure was applied to the fibers. After 24 hr. the water content had decreased to the equilibrium value of 28.0%. Curve B of Figure 2 shows the uptake curve for a small increment of relative humidity 20 min. after the fibers had been subjected to a 79.4%–94.8% RH step. Curve A shows the uptake curve following the same small increment of relative humidity after a wool sample had been left at 94.8% RH for 24 hr. The maximum increase of concentration following the vapor pressure increment is much greater in the former case than for the case where the fibers had reached concentration equilibrium at 94.8% RH prior to the interval absorption step. The final concentration of water in the sample is the same in each case. The fact that the final water concentration shown by Curve B is less than the initial water concentration reflects the overshoot normally observed for a 79.4%–94.8% RH absorption step. Curve C shows the uptake curve following a similar small increment of relative humidity (1.1%) applied after the fibers had been equilibrated at 97.5% RH, so that the initial water content of the fibers would be the same for Curves B and C. It is evident that the maximum absorption attained in Curve B is greater than in Curve C. Therefore the large overshoot illustrated by Curve B is only slightly affected by the initial water concentration and is mainly a function of the time elapsed since the integral sorption was commenced.

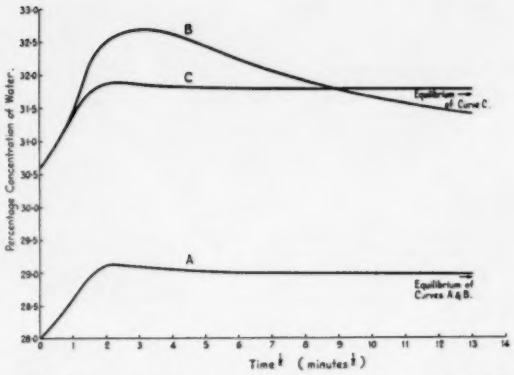



**Fig. 2.** Interval absorption from high initial water concentration. Water uptake vs. (time)$^{\frac{1}{2}}$ for a 1.1% relative humidity step following: Curve A, 24 hr. after a 79.4%–94.8% relative humidity step; Curve B, 20 min. after a 79.4%–94.8% relative humidty step; Curve C, after equilibration at 97.5% relative humidity.

*Comparison of Interval Sorption Data*

Nordon et al. [8] have reported that interval absorption behavior of wool fibers with a high water content shows the same two stages of uptake as exhibited by interval absorption at intermediate concentrations. The first stage of uptake has been described as Fickian and values for the coefficient of diffusion given as a function of relative humidity up to 95% RH. This is contrary to the data presented in Part I and Part II, indicating that for a series of interval absorptions from dry, the second stage of uptake had merged with the first for all absorptions for fibers initially equilibrated with 80% or more relative humidity. In addition no part of the uptake curve could be described as Fickian. It has been stated in the previous section that if the interval absorption followed an integral absorption step, the phenomenon of an absorption overshoot only occurred above 85% RH. However, the initial uptake deviated from Fickian behavior at a much lower relative humidity (*ca.* 80%). Nordon et al. used a vibroscope technique of measuring water content. It has recently been shown by the authors [12] that such a technique yields quite different sorption behavior at high water concentrations. For instance, the equilibrium water concentration obtained at high relative humidities was considerably less than the equilibrium water concentration obtained by weighing fibers on the sorption balance, i.e., different sorption isotherms in the high concentration region are obtained by the two techniques.

For interval absorption steps the amount of water absorbed by the fibers on the sorption balance was usually greater than that absorbed by the fiber in the vibroscope for the same small increment of vapor pressure. However, near saturation the uptake curve obtained by the vibroscope technique also showed an overshoot, and the water contents as measured by the two methods showed closer agreement.

It was also found that, although the equilibrium length of the fiber under tension was practically independent of relative humidity above 80% RH, in this region of high humidities a transient length swelling occurred following small increments of vapor pressure. For instance, for an increase of relative humidity from 85.9% to 88.1%, a Corriedale fiber mounted in the vibroscope increased its length by 0.07% in less than one minute, and slowly reverted to its initial length over a period of several hours. The maximum change of length if used in correcting the amount of water uptake as determined by the vibroscope would represent a correction factor of more than 15% at that time.

Figure 3 shows the uptake curves obtained for the same small increment of relative humidity, 85.9% to 88.1%, for the fibers on the sorption balance (Curve A) and for the fiber mounted in the vibroscope (Curve B). Curve B is uncorrected for longitudinal swelling because of the experimental difficulty of making a quantitative correction during the early stages. However, it will be seen that the calculated change of water content is approximately half by the vibroscope technique and the shapes of the two curves are different.

*Interval Absorption on Horsehair*

In order to examine more closely the shape of a vibroscope uptake curve, a horsehair was substituted for the Corriedale fiber and was subjected to similar treatment. Curve A of Figure 4 shows the uptake curve, corrected for length swelling, following a relative humidity increment of from 85.8% to 88.3%. The longer time of absorption enabled an accurate plot to be made as a function of $(\text{time})^{\frac{1}{2}}$ and for length corrections to be applied. The change in water content was greater than for a Corriedale fiber mounted in the vibroscope but less than for a similar horsehair mounted on a sorption balance (Curve B). It is clear that the initial uptake shows a marked inflection which is indicative of anomalous absorption behavior.

The discrepancy of absorption behavior as determined by the sorption balance and the vibroscope has been the cause of some concern in this laboratory.[1] It is proposed to make a fuller investigation of this problem. Preliminary results have indicated that the effect of the tensioning weight on the fiber in the vibroscope cannot be neglected. It is apparent also that the change of length of the fiber under test can be a cause of error in vibroscope determinations. Watt and Kennett [13] established that the equilibrium weight at zero humidity was variable for fibers mounted on the sorption balance. They showed that it was necessary to relax the fibers in order to obtain reproducible behavior. It is not known as yet what has been the effect of these factors on vibroscope data obtained in this laboratory. It is felt that repeated tests carried out on the same fiber could have brought about a marked change in the sorption behavior.

*Desorption*

Data on the desorption of water from fibers with high initial water concentration, when the relative humidity has been reduced to zero, have been presented by a number of workers. The removal of more than half of the water occurs very rapidly (much more rapidly than the corresponding absorption). However, the shape of the desorption curve is dependent on the size of the desorption step. The behavior in wool and in horsehair is similar but because of the longer time required for horsehair desorption, the effect is more easily demonstrated with that fiber. The curves of Figure 5 illustrate the loss of water as a function of time for desorption steps of varying size, after the horsehair had been equilibrated at 95% RH. The curves obtained following small relative humidity decrements show a sigmoid shape which becomes less marked as the size of the relative humidity change is increased.

[1] The fact that the fiber mounted in the vibroscope is vibrating during a sorption experiment and that this mechanical behavior may modify the sorption properties of the fiber at high humidities has been considered. A series of experiments was carried out in which a fiber was subjected to a large step of humidity from zero to 90%. In one experiment the fiber was vibrated throughout but in the others the vibration was commenced at various stages of the absorption. The differences of the water uptake at various times of the absorption in the experiments lay within experimental error and it was concluded that the vibration of the fibers as obtained in the vibroscope experiments of this laboratory did not modify the sorption behavior.

At lower initial water concentrations it has been shown that the initial loss of water following a small decrease of relative humidity follows Fick's laws of diffusion [11], i.e., the initial rate of water loss was linear as a function of $(\text{time})^{\frac{1}{2}}$. However, it is apparent that Curves A and B of Figure 5 would show an even more sigmoid character as a function of $(\text{time})^{\frac{1}{2}}$ and that desorption from high initial water concentration is non-Fickian for small concentration decrements.

## Discussion

From the data presented in this series of papers it is apparent that the observed kinetic behavior of sorption is markedly dependent on the initial water concentration in the fibers, and also on the length of time the fibers have been at that concentration. Watt and Kennett [13] demonstrated that the molecular organization of keratin changes with time if water is present within the keratin. The extent of such changes is dependent on the water concentration. It is probable that the two phenomena are related, i.e., changes in molecular configuration and changes in kinetic sorption behavior of keratin. Evidence for this is shown in Figure 2 where the effect of the time elapsed after a step change of relative humidity from 79.4% to 94.8% on the kinetic sorption behavior observed for further small step changes of relative humidity is demonstrated. Curve B shows a much greater uptake than Curve A. The elapsed time after the integral relative humidity step was only 20 min. for Curve B, whereas for Curve A 24 hr. had elapsed. The differences between Curve A and Curve B appear to be related to changes which had been occurring in the molecular configuration of the keratin–water complex during the integral absorption step. Furthermore the fact that Curve C, showing absorption from the same initial concentration as Curve B, is similar to Curve A shows that a difference of initial water concentration such as exists between Curves A and B has much less effect on the sorption behavior than the configurational changes in the fibers during sorption.

The change in sorption behavior during an absorption step may be explained in terms of a sol–gel transformation. It has already been proposed [14] that the entry of water into a hydrogen-bonded material breaks a large number of hydrogen bonds, thus disrupting the structure. This breakdown of the hydrogen-bonded structure corresponds to the formation of a sol phase as proposed by Feughelman [3] to explain an initial reduction of longitudinal stress in keratin fibers, following a step change from dry to approximately 90% RH [4]. He proposed that the following increase of longitudinal stress was caused

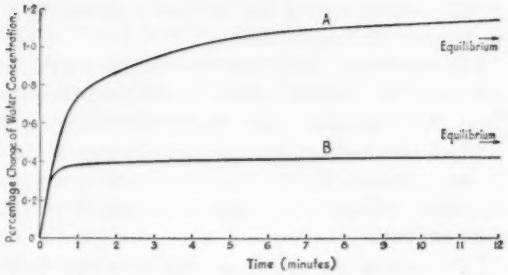



**Fig. 3.** Interval absorption. Water uptake vs. (time) following a relative humidity step from 85.9%–88.1%. Curve A, measured for fibers on a sorption balance; Curve B, calculated for a fiber mounted in a vibroscope.

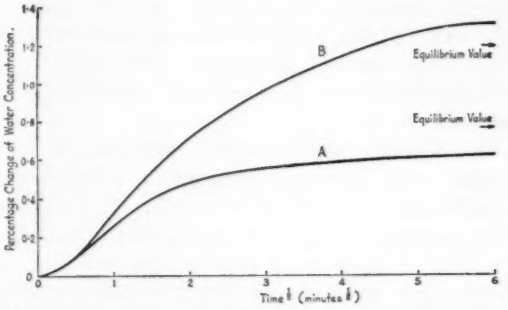



**Fig. 4.** Interval absorption on horsehair. Water uptake vs. $(\text{time})^{\frac{1}{2}}$ following a relative humidity step from 85.8%–88.3%. Curve A, for a horsehair mounted in a vibroscope; Curve B, for a horsehair on a sorption balance.

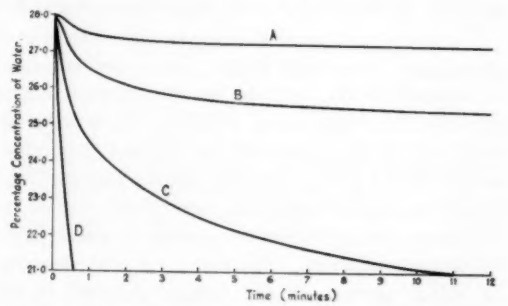



**Fig. 5.** Desorption. Loss of water vs. time following the decrease of relative humidity around a horsehair from 95% to: Curve A, 93.2% relative humidity; Curve B, 90.3% relative humidity; Curve C, 77.3% relative humidity; Curve D, zero humidity.

by a transformation of the sol into a gel by the reformation of hydrogen bonds.

The overshoots above the equilibrium water concentration for sorption steps to relative humidities above 80% coincides with the concentration region in which the mechanical properties of torsional rigidity and longitudinal stress at a fixed small strain pass through a minimum following step changes of relative humidity.

The opening up of the keratin structure during the initial entry of water causes an increase in the effective surface available to water. In the later stages of absorption it is probable that the effective surface for water attachment decreases as a hydrogen-bonded keratin–water complex is formed. Some of the water is then excluded to retain thermodynamic equilibrium between the water in the keratin and the partial pressure of water vapor surrounding the keratin.

In Figure 1 the absorption overshoot is more evident with increasing temperature, although final equilibrium is attained more rapidly. This indicates the possibility that both the breakdown of hydrogen bonding on the entry of water and the build-up of a new keratin–water complex are accelerated by an increase in temperature. However, the breakdown process requires a much shorter time than the reformation process and the increased size of the overshoot would be expected from the greater ease of breaking hydrogen bonds at higher temperatures.

The initial portion of the uptake curve for interval absorption from high initial water concentrations as obtained by the sorption balance shows a marked inflection as a function of $(\text{time})^{\frac{1}{2}}$. Such an uptake curve cannot be accounted for by any generalized form of Fick's laws. Thus we can say that the initial uptake represents anomalous absorption as does also the latter portion where the uptake of water passes through a maximum. Nordon et al. [8] described the initial portion of the uptake obtained by the vibroscope technique at high humidities as Fickian. The uptake curve shown in Figure 4 for a horsehair mounted in a vibroscope clearly shows an inflection and consequently non-Fickian absorption behavior. It is more difficult to trace accurately the course of the uptake curve for a Corriedale fiber in the vibroscope because of the rapid decrease of the rate of uptake to a lower equilibrium value of water concentration than measured on the sorption balance. Nordon et al. made no corrections to their calculated uptake curves for the simultaneous length changes of the fiber. No attempt was made to relax the fibers prior to a series of sorption experiments, nor was any check carried out to determine whether the sorption behavior of the particular fiber had changed during the series of experiments. Evidence that this may have occurred is obtained from the values of diffusion coefficients given by Nordon et al., for the values measured at 25° C. are greater than the values measured at both 5° C. and 35° C. for the same initial concentrations. Watt [11] has shown that the apparent activation energy of diffusion over the same concentration region is 5 kcal./mole. Consequently the coefficient of diffusion would be expected to be higher at 35° C. Comparable interval sorption data has been given by Fujita, Kishimoto, and Odani [5] for several polymer–penetrant systems at temperatures below the glass transition temperature for each polymer. When the polymer was partially crystalline the uptake curve assumed a non-Fickian sigmoid shape at high initial penetrant concentrations.

It appears therefore that the sorption behavior of water into wool (a partially crystalline material) cannot be described as Fickian at high initial humidities irrespective of the technique of measurement.

The interval desorption curves from high initial water concentrations also cannot be fitted by any form of Fick's equation of diffusion. As the size of the desorption step is increased the shape of the desorption curve approached closer to the shape expected if Fick's laws were being obeyed. However, this would seem to be merely a coincidence as the rate of desorption changed from being less than that predicted by a Fickian equation to a faster rate. For large desorption steps the initial rate of desorption is approximately linear with time and is faster than the corresponding rate of absorption.

Therefore both absorption and desorption to and from high water concentrations in wool is anomalous. However, there is more involved than what has normally been referred to as anomalous diffusion, the distinguishing features of which are that the uptake curve shows an inflection as a function of $(\text{time})^{\frac{1}{2}}$ and the initial rate of desorption is faster than the initial rate of absorption. Additional deviations from Fickian behavior are the concentration overshoots on absorption and the sigmoidal desorption curve for small decreases of water vapor pressure.

The occurrence of concentration overshoots on absorption has been shown to be consistent with a keratin–water complex readily altered by the breaking and re-formation of the weak interchain bonds. Further evidence of the ability of the keratin–water complex to change readily in the radial direction is given by measurements of radial compressibility. Denby [1] has shown that the radial compressibility of wool fibers varies by a ratio of 19 : 1 for dry fibers as compared with wet fibers. There is also some creep in this value for wet fibers, in that, if compression is measured 2 min. after the load is applied, the ratio for dry and wet fibers is then 27 : 1. This high ratio demonstrates the structural weakness radially of wet fibers. It is apparent from the occurrence of creep that structural changes can take place readily in fibers with a high concentration of water.

On absorption into polymers there is expansion of the network as the concentration gradient moves through the keratin. For desorption there is no moving concentration gradient, but rather a steep gradient is set up rapidly at the surface, and the concentration within the sorbent decreases more or less uniformly [6, 7]. It is probable that the structure then collapses and takes up a new equilibrium keratin–water configuration, in the manner proposed by Smith [9] and White and Eyring [15].

Thus both the absorption and desorption behavior of keratin, with high water concentrations, reflect the ease of structural change within the keratin–water complex. Entry and exit of water from keratin is partially governed by structural changes which are occurring during sorption, and the sorption cannot be adequately described by a Fickian mechanism, excepting for water concentrations below 2.5%. Sorption can be partially described using Fick's laws of diffusion for water concentrations in the fibers of between 2.5% and 19%. At higher water concentrations, Fick's laws of diffusion cannot be used to give an accurate description of the wool–water sorption behavior, and molecular configuration assumes a more important role.

## Acknowledgment

The authors are indebted to Mr. R. M. Rabbidge, who designed the type of vibroscope used in this work.

## Literature Cited

1. Denby, E. F., TEXTILE RESEARCH JOURNAL **31**, 69 (1961).
2. Downes, J. G. and Mackay, B. H., *J. Polymer Sci.* **28**, 45 (1958).
3. Feughelman, M., *J. Appl. Polymer Sci.* **2**, 189 (1959).
4. Feughelman, M. and Robinson, M., *J. Appl. Polymer Sci.* **1**, 371 (1959).
5. Fujita, H., Kishimoto, A., and Odani, H., *Progr. Theoret. Phys. (Japan)*, Suppl. No. 10, 210 (1959).
6. Long, F. A. and Richman, D., *J. Am. Chem. Soc.* **82**, 513 (1960).
7. Long, F. A. and Watt, I. C., *J. Polymer Sci.* **21**, 554 (1956).
8. Nordon, P., Mackay, B. H., Downes, J. G., and McMahon, G., TEXTILE RESEARCH JOURNAL **30**, 761 (1960).
9. Smith, S. E., *J. Am. Chem. Soc.* **69**, 646 (1947).
10. Watt, I. C., TEXTILE RESEARCH JOURNAL **30**, 443 (1960).
11. Watt, I. C., TEXTILE RESEARCH JOURNAL **30**, 644 (1960).
12. Watt, I. C. and Algie, J. E., to be published.
13. Watt, I. C. and Kennett, R. H., TEXTILE RESEARCH JOURNAL **30**, 489 (1960).
14. Whaba, M. and Nashed, S., *J. Textile Inst.* **48**, T1 (1957).
15. White, H. J. and Eyring, H., TEXTILE RESEARCH JOURNAL **17**, 523 (1947).

*Manuscript received January 23, 1961.*

# Wrinkle Resistant Properties of Dialdehyde Cotton

**Charles H. Mack and Wilson A. Reeves**

*Southern Regional Research Laboratory,[1] New Orleans, La.*

**Abstract**

The effect of periodic acid oxidation on the wrinkle resistance of cotton fabric has been investigated. In the range of oxidation where basic fabric properties are preserved the dry WRA increases with increasing oxidation. The change in wet WRA for these fabrics is negligible, suggesting that cross-links which are evident in the dry state are broken in the presence of water. An explanation involving hemiacetal and hemialdal formation is advanced.

SEVERAL investigators have reported changes in the physical characteristics of cotton cellulose which had been treated with periodic acid solutions. Such treatment oxidizes the glycol portion in the 2,3-position of the anhydroglucose unit to the corresponding 2,3-dialdehyde. Davidson [3] conducted an extensive study of the physical changes imparted to cotton cellulose by this treatment but no mention was made regarding wrinkle resistance. Our investigation has revealed improved wrinkle resistant properties in cotton fabrics which have been oxidized with periodic acid. Dialdehyde cotton is extremely sensitive to alkali, including mild soap solutions; therefore it is not likely to be used in fabric for its wrinkle resistant properties unless the fabric is restricted to dry cleaning. It is believed that the fundamental implications involved in this phenomenon may be of value in developing a better understanding of wrinkle resistant fabrics.

## Materials and Methods

The work reported herein was carried out on a desized, scoured, and bleached 80 × 80 print cloth weighing 3.1 oz./yd.$^2$. Five samples of this fabric were oxidized in periodic acid solutions (pH 1.8) at room temperature.

The oxidations were carried out to varying degrees under different conditions. The results will be described in a later section.

The wrinkle recovery angle (WRA) was determined on both the dry and wet fabrics. Dry wrinkle recovery was determined according to the ASTM Monsanto method [2]; the wet determinations were made according to the procedure of Lawrence and Phillips [6]. Moisture regain was obtained by heating the samples for 2 hr. at 70° C. and equilibrating for 72 hr. at 65% RH at 30° C. The equilibrated samples were weighed, dried for at least 4 hr. at 105° C., and again weighed. Percent moisture regain was calculated as the percent change in weight. The dry density of the samples was determined according to the procedure reported by Orr et al. [7] which utilizes the gradient column technique.

The potassium bromide wafer technique was used to obtain the infrared spectra [10].

## Results and Discussion

A description of the periodic acid oxidized fabric samples used in this study is given in Table I. The extent of oxidation as determined by the amount of periodic acid consumed and by the sodium borohydride reduction method is shown for each of the five samples. Percent moisture regain, percent shrinkage, and weight gain data for each of the fabric samples are also included.

The data in Table I reveal that a rather wide spread of oxidation ranges was obtained in the various samples. Although the agreement between the percent oxidation as calculated by periodic acid consumed and that determined by the borohydride reduction method is not very good, there is sufficient indication that the major amount of the oxidizing agent was used to form the dialdehyde material. The shrinkage and moisture regain data agree with observations made by Davidson [3] that shrinkage and moisture absorption increase with increasing

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

oxidation. This increase in moisture absorption presumably accounts for the percent weight gain which was observed.

The two most highly oxidized samples were very stiff and yellow, while the other three samples exhibited no noticeable stiffness and only a light yellow color. The strengths of the various fabrics decreased with increasing oxidation. These results also agree with those of Davidson, who found that acid hydrolysis does not play an important part in the oxidation of cellulose by periodic acid. The loss in strength is probably due to the change in structure of the anhydroglucose polymer and not to the formation of hydrocellulose.

Infrared spectra were obtained for each of the five oxidized samples as well as for untreated cotton for comparison. The resulting curves of the oxidized samples were similar to those reported by Rowen et al. [12], who suggested that the aldehyde groups in the oxidation product were readily hydrated to explain the absence of a strong C=O stretching vibration at about 1730 cm.$^{-1}$. A moderately strong band appeared at about 1630 cm.$^{-1}$ which has been attributed to the OH deformation mode characteristic of adsorbed water [15], as well as a peak in the 900 cm.$^{-1}$ region, to which a definite assignment is in dispute [13].

Another sample of oxidized fabric, which analyzed 17% dialdehyde content, was prepared for infrared analysis by grinding in a Wiley mill, then mixing with the potassium bromide, preparatory to making the disc. This mixture was divided into three equal portions and stored at different relative humidities for three weeks at room temperature. The discs were then prepared and the infrared curve run on each sample, concentrating on the 1600–1800 cm.$^{-1}$ region. The results are shown in Table II.

In the C=O absorption region at *ca.* 1730 cm.$^{-1}$ the absorptivity increased when the sample was stored under atmospheres containing less moisture. A corresponding decrease in OH stretching due to adsorbed water at *ca.* 1640 cm.$^{-1}$ occurred. These results agree with those of Higgins [5], who suggests that the development of a C=O band (i.e., a free aldehyde group) when the oxidized sample is dehydrated lends support to Rowen's suggestion that the aldehyde groups are readily hydrated.

Spedding [13] states that phosphoric anhydride drying of periodate oxidized cellulose dehydrates the hydrated aldehyde, $-CH(OH)_2$, since he finds a

**TABLE I. Periodic Acid Oxidation of Cotton Fabric**

| Sample No. | Oxidation time, hr. | Mols. $HIO_4$ available per 100 anhydroglucose units | Mols. $HIO_4$ consumed per 100 anhydroglucose units | Dialdehyde content ($NaBH_4$ method),* % | Shrinkage, % | | Moisture regain, % | Wt. gain, % |
|---|---|---|---|---|---|---|---|---|
| | | | | | Warp | Fill† | | |
| 1 | 48 | 116 | 73 | 58 | 28 | 25 | 9.80 | 4 |
| 2 | 24 | 56 | 47 | 40 | 17 | 12 | 11.58 | 3 |
| 3 | 17 | 24 | 19 | 17 | 6 | 3 | 7.43 | 1 |
| 4 | 24 | 5.8 | 5.7 | — | 3 | 2 | 7.08 | 1 |
| 5 | 24 | 1.1 | 1.1 | — | 3 | 0 | 6.85 | 1 |

* The sodium borohydride method of analysis for dialdehyde contents [9] of less than 10% oxidation is impractical.
† The fabric was treated in the slack condition because tension affects the level of oxidation [7].

**TABLE II. Infrared Absorption Data on Periodate Oxidized Cotton ***

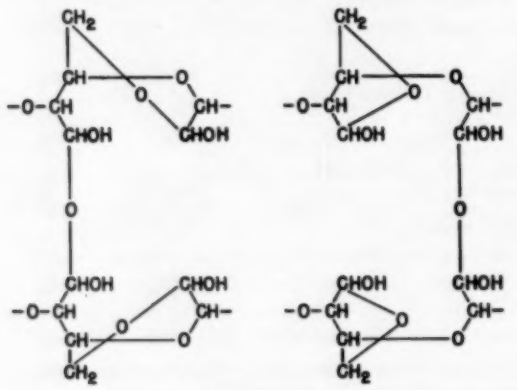
| Sample No.† | Storage‡ relative humidity, % | Wave No., cm.$^{-1}$ | Absorptivity | Wave No., cm.$^{-1}$ | Absorptivity |
|---|---|---|---|---|---|
| 1 | 65 | 1730 | 0.833 | 1637 | 19.115 |
| 2 | 20 | 1727 | 2.385 | 1639 | 9.370 |
| 3 | ** | 1730 | 3.425 | 1637 | 7.021 |

* Dialdehyde content of the oxidized cotton sample analyzed 17%.
† Sample was intimately mixed with KBr, divided into three equal portions, each stored at stated relative humidities before compressing into final disc.
‡ Samples were stored at relative humidities shown for three weeks at room temperatures.
** Sample was stored over $P_2O_5$.

further increase in carbonyl intensity (free —CHO) upon heating the sample. He concludes that the intermediate and more stable form is the hemialdal form, —CH(OH)—O—CH(OH)—.

Comparison of the infrared curves of the five oxidized samples previously mentioned in the 3400 $cm.^{-1}$ (OH stretching) region shows a decrease in percent transmittance as the oxidation increased. The curve obtained by plotting the extinction coefficient at 3400 $cm.^{-1}$ of the oxidized samples against the percent oxidation was a straight line. Extrapolation of this curve to 100% oxidation yielded an extinction coefficient which would be expected for a sample containing one and one-half to two hydroxyl groups per repeating unit. The only structure that fits this observation, as well as the infrared data, would be a cyclic hemiacetal-hemialdal mixture. The reports of Smith and coworkers [1] and Honeyman [4] on various periodate oxidized carbohydrates, as well as those of Nevell [9] and Spedding [13] on oxycellulose, suggest the presence of both hemiacetals and hemialdals in periodate oxidized carbohydrates.

Two such possible structures are shown below:



These structures will be discussed later to explain some of the wrinkle resistant properties of these fabrics.

The effect of periodate oxidation on the wet and dry wrinkle recovery angles of cotton fabric is shown in Figure 1. The dry wrinkle recovery angle (WRA) curve reaches a maximum at the 20–30% oxidation range. Examination of the two most highly oxidized samples revealed that other factors probably affected the wrinkle resistance. It was pointed out previously that these fabrics were stiff and discolored while the other samples retained

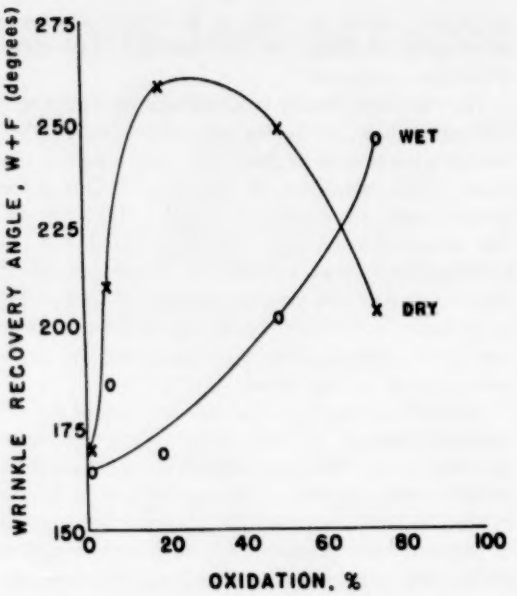



Fig. 1. The effect of periodate oxidation on wrinkle recovery.

normal fabric appearance. For the three less highly oxidized samples, the dry WRA increased with increasing oxidation, suggesting the presence of a cross-link between polymeric chains. For these same samples the wet WRA was negligible, suggesting a water-sensitive cross-link. Although none of the fabrics are completely insoluble in cuprammonium solution, the oxidized fabrics are more slowly soluble than the untreated control cotton fabric. The hemiacetal and hemialdal linkages, postulated above, are most likely involved in the cross-linking. Both hemiacetals and hemialdals participate in a reversible equilibrium in solution to form the free carbonyl and the alcohol or water. However, in the cellulose system it is more probable that the hemialdal linkage would be readily hydrated as shown:

$$—CH(OH)—O—CH(OH)— \overset{HOH}{\rightleftharpoons} —CH(OH)_2+CH(OH)_2—$$

The effect of periodic acid oxidation on the dry density of cotton fabric is shown in Figure 2. It is evident that as the degree of oxidation increases the dry density decreases. The dry density is a measure of the compactness or degree of openness of the fiber since it is the weight in grams per cubic centimeter. Thus, the oxidation has produced a more open struc-

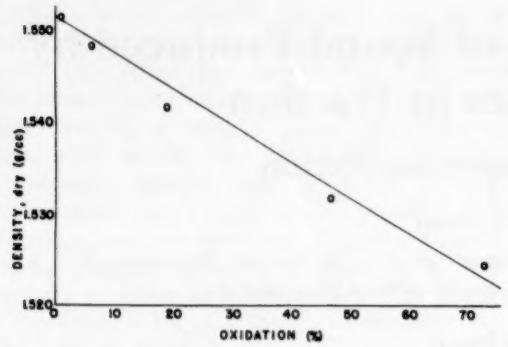



**Fig. 2.** The effect of periodate oxidation on dry density.

ture. The dry density of acetylated cotton has been shown to decrease linearly as the degree of substitution increases [7]. Recently it was found that cotton treated with a cross-linking agent (dimethylolurea) was less dense than that treated with a similar monofunctional derivative (monomethylolurea) [14].

Work is in progress to modify, chemically, dialdehyde cotton fabric with polyfunctional aldehyde reagents capable of cross-linking. This type of modification should render the fabric insoluble in alkaline reagents and also increase the dry and wet WRA of the fabric.

## Acknowledgment

The authors are indebted to workers at the Northern Utilization Research and Development Division for carrying out the oxidations on the cotton fabric, and to R. T. O'Connor of this laboratory for the infrared determinations.

## Literature Cited

1. Abdel-Akher, M. and Smith, F., *J. Am. Chem. Soc.* **81**, 1718–1721 (1959).
2. American Society for Testing Materials, Philadelphia, Pennsylvania, A.S.T.M. Designation, D1295–53T.
3. Davidson, G. F., *J. Textile Inst.* **32**, T109–131 (1941).
4. Guthrie, R. D. and Honeyman, J., *Chemistry & Industry* **1958**, 388–389.
5. Higgins, H. G. and McKenzie, A. W., *Australian J. Appl. Sci.* **9**, 167 (1958).
6. Lawrence, E. W. and Phillips, R. H., *Am. Dyestuff Reptr.* **45**, P548–550, P561 (1956).
7. Orr, R. S., Weiss, L. C., Moore, H. B., and Grant, J. N., TEXTILE RESEARCH JOURNAL **25**, 592–600 (1955).
8. Nevell, T. P., *J. Textile Inst.* **47**, T287–297 (1956).
9. Nevell, T. P., *Chemistry & Industry* **1958**, 389–390.
10. O'Connor, R. T., DuPré, E. F., and McCall, E. R., *Anal. Chem.* **29**, 998–1005 (1957).
11. Rankin, J. C. and Mehltretter, C. L., *Anal. Chem.* **28**, 1012–1014 (1956).
12. Rowen, J. W., Forziati, F. H., and Reeves, R. E., *J. Am. Chem. Soc.* **73**, 4484–4487 (1951).
13. Spedding, H., *J. Chem. Soc.* **1960**, 3147.
14. Steele, R. and Schiwall, R. P., TEXTILE RESEARCH JOURNAL **29**, 228–234 (1959).
15. Tsuboi, M., *J. Polymer Sci.* **25**, 159–171 (1957).

*Manuscript received January 23, 1961.*

# The Spectral Distribution of Sound Produced by Fibers and Fabrics in Friction

## Part I: Improved Instrumentation

**Walter J. Thorsen**

*Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany 10, California*

**Paul Veneklasen**

*Western Electro-Acoustic Laboratory, 11789 San Vicente Boulevard, Los Angeles 49, California*

### Abstract

The constructional details and theory of operation of a highly stable and sensitive fiber and fabric friction sound analyzer are described. Sound pressure curves for three typical fabrics and one bulk wool are shown. Results will be described in detail in Part II.

### Introduction

Preliminary experiments conducted at this laboratory [1] [1] have indicated that information on wool fiber and fabric quality related to "handle" can be derived by the analysis of the spectrum of sound produced by these materials in friction. Each material produces a spectrum, which, being a characteristic of the material, is an important index of its quality. From experience gained by operating the original acoustic equipment it was concluded that the system could be improved in its operating facility and accuracy through several modifications. In research conducted under a contract,[2] the requirements which were developed for this improved instrument were:

1. The instrument should be able to accept fibers, as well as fabrics.
2. These materials should be tested in a continuous manner so that the continuous production of sound affords ample time for sound-spectrum measurements.
3. It should be possible to rub fabrics against themselves or any other selected surface.
4. The pressure induced on, between, or in the fibers or fabrics should be evenly distributed and be variable, from 0.03 to 2.0 lb./in.$^2$.
5. All segments of the frictional interface must move at the same relative velocity. Means shall be provided to vary this velocity. In the case of fibers, a gentle, continuous shearing action should occur.
6. The sound vibrations produced shall be picked up and converted to a voltage nearly proportional to sound pressure over a range of from 20 to 5,000 cycles per second, with an accuracy of 0.5 decibel.
7. The instrument must be stable in its calibration over long periods of time and satisfactorily isolated from external noise and vibration.

All of these requirements were fully met by the contractor and a description of the instrument [2] is given below, along with some test results.

### Construction Details

#### *Method of Causing All Interfacial Elements to Move at the Same Relative Velocity*

The equipment is designed to hold two cloth samples—both circular. One, 3.6 in. in diameter, is clamped in a movable upper cloth-holding assembly, herein termed the "upper head," and the other, 1.9 in. in diameter, is clamped in a fixed lower cloth-holding assembly, herein termed the "lower head." The two cloth samples are rubbed against each other

[1] Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture, Albany 10, California.

[2] Conducted by Western Electro-Acoustic Laboratory under contract with United States Department of Agriculture.

by means of the motion of the upper head, as described below, and shown in Figure 1. Synchronous motor (A) drives idler gear assembly (B) by a three-speed timing belt, timing gear combination. Assembly (B) in turn drives two equal-diameter gears which in turn drive two identical discs (C) at the same angular velocity. Each disc (C) supports a smaller disc (D), in turn supporting a pivot. The offset radius of these pivots may be adjusted by rotating discs (D). Setting of discs (D) is facilitated by a pointer-scale arrangement. Both discs are clamped at the same radius by thumb screws. The crossarm of the upper head (E) rides on these pivots and a motion is produced which may be described as both linear and orbital, i.e., the head rotates in a plane about a point but does not rotate about its own axis. Hence, all segments of the sample interface move at the same relative velocity.

The above technique causes the area of cloth being rubbed to remain the same. In addition, this sound-generating area remains at a constant distance from a pick-up microphone which is placed below the sample in the lower head.

Since the offset radius of the pivots is variable between zero and 0.5 in., orbital velocities of from zero to 320 mm./min. are attainable with the three-speed drive.

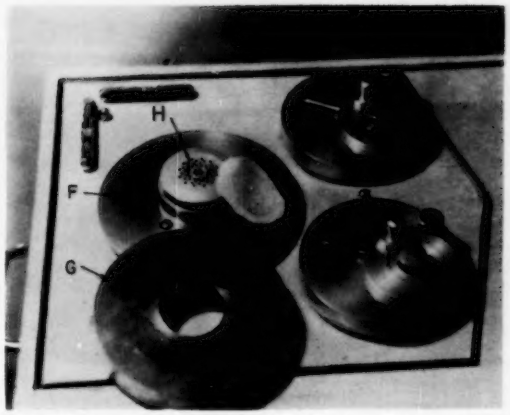



**Fig. 2.** Lower head with cloth-clamping disc removed. Microphone is directly under the grid.

*Cloth-Holding Technique*

Figure 2 shows the lower head (F) with its cloth-clamping disc (G) removed. The disc of cloth shown is laid on grid (H) and clamped by the disc. The microphone is directly under the grid. Upper head (E) with its cloth-clamping ring is shown in Figure 6. Also shown in this figure are details of a 150-gauge Mylar diaphragm, backed by liquid which acts to distribute evenly the pressure induced in the fabrics by the weight of the head. Flatness in

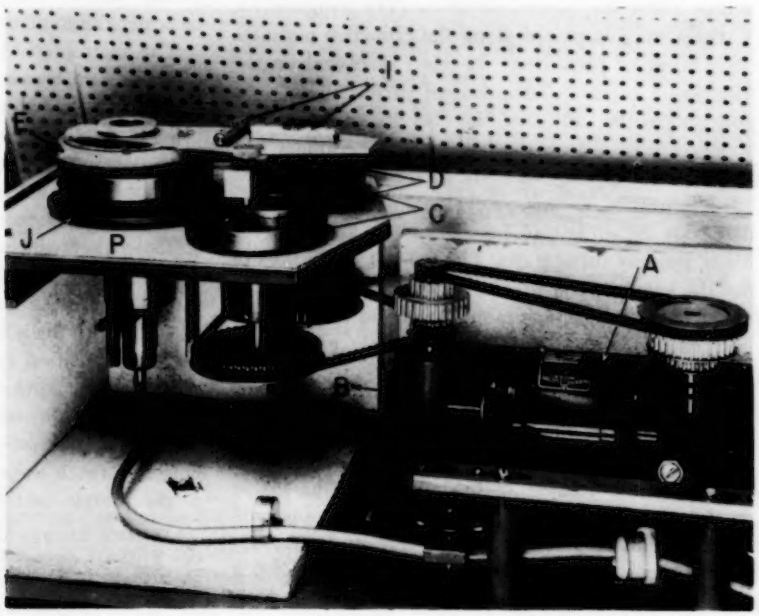



**Fig. 1.** View of fiber and fabric friction sound analyzer with covers removed to show working parts.

**Fig. 3.** Lower head with grid removed, showing microphone placement in sound cavity. A Mylar diaphragm may be substituted for the grid.

the diaphragm is maintained by the setting of a rear filling plug. Other materials such as screening, gauze, rough-surfaced films, etc., may be held by the upper head and used as standard sound-generating surfaces.

*Method of Varying the Pressure Exerted on the Textile Samples*

Pressure is applied to the fabrics by the force-moment of the weight of the head-crossarm assembly, acting about the pivots on discs (D) (Figure 1). Various weights placed along the crossarm permit a wide range of pressures. Levels (I) placed on the instrument cabinet and crossarm permit these components to be adjusted for levelness. Leveling screws are placed on the bottom of the cabinet and one is placed at one end of the crossarm to adjust for the levelness of its axis. Levelness of the perpendicular axis is adjustable by raising or lowering the lower head by turning disc (J). Thus, regardless of the thickness of the textile material under test, the upper head may be maintained level and the pressure induced in the sample can be accurately gauged.

*Method of Testing Bulk Wool*

In testing bulk wool, a metal disc $\frac{1}{8}$ in. thick is inserted in place of the cloth in the upper head. The disc is a little smaller in diameter than the inside diameter of the clamping ring, and the clamping ring is screwed in only to the point where its lower surface matches the lower surface of the disc. Then a double-coated disc of cellophane tape is placed on this lower surface, holding the disc in place. A "ball" of the bulk wool (0.3 g. or more) is laid on the lower head and clamped at its edges by the lower clamping disc. Then the upper head is laid gently on top of the wool, thereby adhering to it. The orbital radius is then set to approximately 0.1 in. to produce a gentle shearing action in the bulk wool. In this manner the sound produced is generated only by the fibers rubbing against one another inside the wool sample. A similar action could be produced in cloth.

*The Microphone and its Accessories*

In Figure 3 the grid holders (K) and grid (H) have been removed to show the placement of the microphone (L) in the sound cavity. The grid, which seats directly over the microphone, may be replaced by a thin (usually 50-gauge) Mylar diaphragm.

When the grid is used during a test the grid supports the lower sample and transmits the sound generated through its holes directly to the microphone cavity. When the diaphragm is used the sound produced in the fabrics is picked up by the diaphragm and then transmitted to the cavity. An additional effect of the diaphragm is that the vibrations of the fabrics as a whole are also picked up, since the lower fabric rests on the diaphragm, which is highly compliant. Thus the grid and diaphragm offer two basically different modes of testing textile materials.

The microphone [3] is a precision, laboratory-type condenser microphone which is suitable for use as a primary standard in acoustic research. It is extremely stable, highly sensitive, and has a level frequency response from 20 to 5000 cycles/sec. The microphone is screwed into a preamplifier directly below it. Associated with the preamplifier is an acoustic filter which consists of three air cavities interconnected with narrow tubes. These tubes give the necessary leak for static air pressure that builds up in front of the microphone when the upper head is placed in position for a test. In addition the filter, which has a low cut-off frequency, cuts out any airborne motor noise approaching from below. Therefore, the only path remaining for external noises to reach the microphone is through the edges of the sample under test.

[3] Western Electric Model 640 AA. Mention of commercial products does not constitute recommendation by the Department of Agriculture over others of a similar nature not mentioned.

The microphone preamplifier is connected to a line amplifier. This amplifier raises the level of the microphone signal 40 db. and at the same time supplies a constant polarizing voltage to the condenser microphone. The output of the line amplifier is then fed into a wave analyzer. The purpose of the analyzer is to select narrow bands of the sound spectrum for study. Thus by sweeping over the whole spectrum a "picture" of the acoustic properties of textile materials is obtained.

*Isolation of the Microphone from Internal and External Vibrations*

The main surface plate (P, Figure 1), on which the microphone components are mounted, is isolated from motor vibrations by isomode (rubber) supports. The motor is also "floated" on such supports (see Figure 1) to minimize the imparting of vibrations to the frame of the instrument. Building vibrations are attenuated by a series of supports consisting of tennis balls resting in wooden sockets.

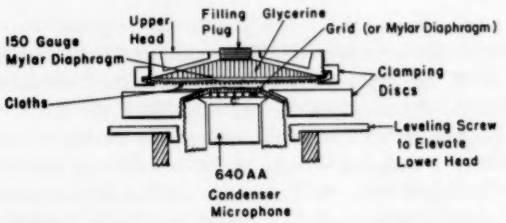



**Fig. 4.** Cut-away diagram of upper and lower head.

The first such support is directly under the instrument itself. To further dampen possible vibrations a heavy metal plate is placed between this support and the instrument. This first support rests on the bottom of a small inner anechoic chamber, which is lined with acoustic tile. This inner chamber rests on tennis-ball supports on the bottom of an outer, larger anechoic chamber. This larger chamber is "floated" on rubber stoppers.

To reduce friction noises generated by the shafts of discs (C, Figure 1), Teflon bearings are used.

*Acoustical Design*

When two cloths are rubbed against one another, the interfacing fibers are set in vibration. Thereby a sound is generated, characterized by the length, thickness, mass, and elasticity of the fibers. Various elements of the cloth will also be vibrated and these vibrations will be a function of yarn and fabric construction. Both types of vibration can be felt and are normally referred to as the "handle" of the cloth. Therefore, a correlation between the sound from the vibrating fibers and the "handle" of the cloth must exist.

With the instrument described herein it is possible to measure only the fiber sound or a combination of fiber sound and the vibrations of larger elements in the cloth. As shown in Figure 4 both are measured as the sound pressure in a small cavity (C′) which is directly over the condenser microphone. When the lower sample is supported by a grid only the fiber sound will produce pressure variations in the cavity. However, when, instead of a grid, the lower sample is supported by a thin Mylar diaphragm, the vibrations of this diaphragm will be determined by the vibrations of the lower surface of the sample plus the fiber sound.

*Limitations*

An analysis of the acoustical circuit consisting of the microphone, the cavity in front of it, the cloth samples, and grid or diaphragm, shows that the measured sound pressure may not be a true representation of the fiber sound and cloth vibrations because of the following factors: (a) acoustical resonances in the cavity at high frequencies; (b) diaphragm resonances at high frequencies; and (c) leak-off of the fiber sound through the edges of the cloth (or fibers) at low frequencies.

However, the acoustical resonances in the cavity have been minimized by designing the cavity as small as practical. This, at the same time, produces an increased sensitivity of the instrument. In addition the cavity's wall is cone shaped, which also tends to minimize resonances.

Diaphragm resonances were checked by transmitting a known sound spectrum into the cavity with a calibrated crystal transducer. An analysis of the sound pressures produced, as picked up by the microphone, shows the following:

1. The compliance of the diaphragms (50–300 gauge Mylar) is much higher than the compliance of the air cavity between the diaphragm and the microphone.
2. The sound pressure drops off at low frequencies due to the leak for static pressure.

3. The gauge 300 Mylar diaphragm has its resonant frequency at approximately 3 kc., while the gauge 50 Mylar diaphragm has its resonant frequency at 7.1 kc.

Since the compliances of the Mylar diaphragms are so large in relation to the compliance of the air cavity, their influence on the diaphragm resonances is practically nil. This fact makes the use of diaphragms quite reliable, since very little care is required in clamping a diaphragm in the lower head to obtain the same diaphragm compliance.

When cloths are being tested, an additional compliance enters the picture, namely the compliance of the cloth samples. Diaphragm resonant frequencies are shifted downward, and in addition they are more damped. However, it has been found that reliable sound-pressure measurements may still be carried out in the frequency range below 5 kc.

Leak-off of the fiber sound through the edges of the cloth or fibers may be corrected for by the use of the previously mentioned crystal transducer. If the acoustic impedance through the edges of the cloth samples is a pure flow resistance (tight weaving), the pressure will drop off at a rate of 6 db./octave below the frequency where the impedance of the cavity is equal to the flow resistance. If, on the other hand, the leak impedance is a pure air mass (loose weaving), the pressure will drop off at a rate of at least 12 db./octave below the resonant frequency between the acoustic compliance of the cavity and the air mass in the edges of the cloth samples.

In practice the leak impedance will be a mixed flow-resistance–air-mass. Figure 5 shows the theoretical response curves for these various conditions. Sound pressure at the microphone is plotted as a function of frequency, assuming the presence of a constant-pressure sound source. The upper curves represent fabric acoustic impedances approaching a pure air mass, while the lower curves represent impedances approaching a pure flow resistance. The central curves represent nearly equal mixtures of both.

In order to determine the actual response curve for a fabric under test, the transducer is placed on top of the upper cloth sample. Since the transducer weighs the same as the orbiting head, the fabric is compressed or compacted exactly as during a test. When a constant voltage of 5.0 volts is fed into the transducer and the frequency varied, a measured response curve such as is shown in Figure 6 (dotted line) for a wool flannel will be obtained. This curve must be corrected for the non-linearity of the transducer response curve, and the resultant corrected curve is shown below the measured curve. Finally, a correction must be made for the fact that the

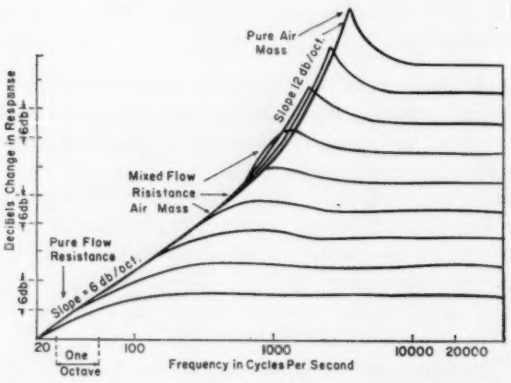



**Fig. 5.** Response curves for fabric acoustic impedances ranging from a nearly pure air mass to a nearly pure flow resistance.

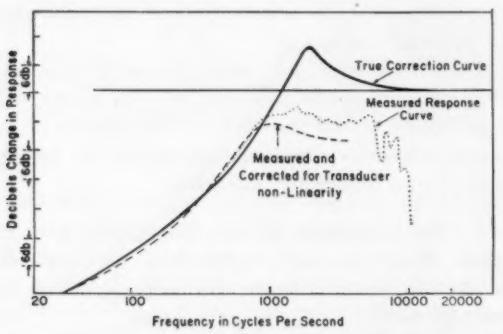



**Fig. 6.** Measured and correction curves for leak through a wool flannel.

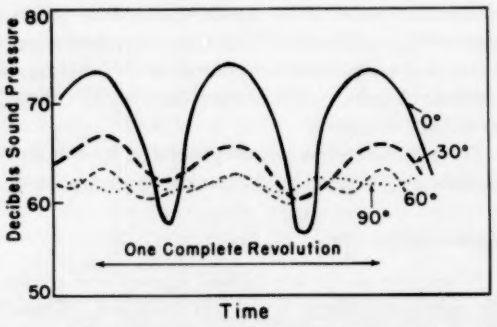



**Fig. 7.** Effect of relative orientation of weave ridges of a fabric on variability of sound pressure as upper head orbits.

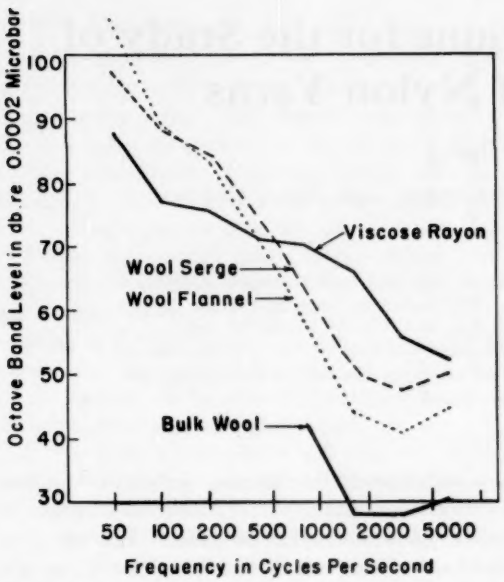



**Fig. 8.** Sound pressure spectra produced by various textile materials, using the grid.

volume of the cavity is increased by the volume of the transducer, producing an apparent low sensitivity. This volume is approximately 6.75 cm.$^3$ and the volume of the cavity alone is only 1.52 cm.$^3$, making a total volume of 8.27 cm.$^3$ plus the air volume in the cloth samples above the grid. The fractional increase in volume when the upper head is replaced by the transducer is:

$$\frac{8.27 + t \times 7}{1.52 + t \times 7} \quad (t \text{ in cm.})$$

where $t \times 7$ is the air volume of the cloth samples above the grid. The number 7 is the area of the samples, while $t$ is the effective thickness of the two samples. By substituting the increase in volume into the equation

$$\text{db.} = 20 \log \text{ (fractional increase in vol.)}$$

the magnitude of the decibel decrease in sensitivity due to this increase is calculated. Therefore the "true correction curve" (see Figure 6) is the one which is this number of decibels above the "corrected for transducer non-linearity" curve. This true correction curve is obtained from Figure 5 by superimposing a transparent version of Figure 5 over Figure 6. Interpolation may be necessary. Therefore in order to obtain the true sound spectrum of a fabric the "true correction curve" of Figure 6 must be added to the uncorrected sound pressure curve.

*Influence of Relative Weave Orientation on Variability of Sound Pressures Produced*

The sound generated by fabrics at all frequencies produces two maxima and two minima for each orbit of the upper head. The magnitude of each maximum and minimum is a function of the relative orientation of the weave ridges of the two samples as shown in Figure 7.

*Sound Pressures Generated by Various Fabrics*

The spectral distributions of sound produced by typical wool flannel, wool serge, rayon, and bulk wool were measured. (A complete description of results obtained with a wide range of textile materials is to be published in Part II.) Orbital velocity was 320 mm./min. and the interfacial pressure was 0.306 lb./in.$^2$. To achieve a minimum variation in sound pressure the weaves were oriented perpendicular to one another. As is customary in acoustics, the variations were averaged mentally at each octave band. These averages were converted to sound pressure; the results with the grid are shown in Figure 8. It is seen that the various textile materials produce widely varying sound spectra under the same conditions of test.

During each test the background noises were also determined. It was found that with all fabrics the background noises were more than 10 db. below the measured curves. This means that any corrections for such noises would be 0.4 db. or less in magnitude and therefore negligible. However, with bulk wool a correction is necessary below 100 cycles/sec. with the diaphragm and below about 1000 cycles/sec. with the grid, since the openness of this material permits the various noises to reach the microphone. Measurements are not possible below about 500 cycles/sec. with the grid.

## Literature Cited

1. Thorsen, W. J. and Lundgren, H. P., *Proc. 1955 Internat. Wool Textile Res. Conf. Aust.* **E294** (1956).
2. Veneklasen, Paul S. and Jorgensen, Finn, U. S. Patent No. 2922303 (January 26, 1960).

*Manuscript received February 8, 1961.*

# A New Staining Technique for the Study of Skin and Core of Nylon Yarns

**W. Rhett Berry**

*Research Division, American Enka Corporation, Enka, North Carolina*

## Abstract

A new technique for the differential staining of skin and core structure of nylon 6 and 66 yarn cross-sections has been developed. The technique requires the use of two water-soluble dyes, Kiton Pure Blue V, an acid dye, and Methyl Violet 2B Supra I, a basic dye. With these two dyes there is no chemical swelling of the cross-section as with $ZnCl_2$, iodine staining. Also the skin of an undrawn filament, which is reported by some investigators to be undetectable, can be stained.

## Introduction

For many years a number of investigators have studied the skin and core structure of rayon filaments by a number of staining techniques. This type of differential staining of skin and core has been most useful in the study of spinning schemes and their effects on physical properties, in the identification of yarns, and in accounting for many of the differences observed in the end uses of the fibers.

It was thought that a staining technique for the investigation of skin and core structure might prove an equally valuable tool for the study of nylon variables. Therefore, efforts were made to develop a satisfactory staining technique that would differentiate between the skin and core of a nylon filament without chemically swelling or otherwise damaging the yarn cross-section.

Previous investigators have demonstrated the presence of a skin-type structure on nylon by first swelling the yarn cross-section in $ZnCl_2$ and then staining the skin with iodine.[1] This type of staining leaves much to be desired, as far as an accurate determination of the amount of skin is concerned, since the $ZnCl_2$ chemically swells both the skin and core but possibly to different degrees; and, too, continued treatment with the $ZnCl_2$ will ultimately disintegrate the nylon sections.

A number of alcohol- and water-soluble dyes were investigated to determine their affinity for nylon cross-sections and their ability to differentiate between skin and core of the nylon filament. By using a combination of two water-soluble dyes, a satisfactory and reproducible staining technique has been developed for staining the skin–core structure of both nylon 6 and nylon 66 yarns. The two dyes used in this case were Kiton Pure Blue V, an acid dye, and Methyl Violet 2B Supra I, a basic dye.[2]

[1] See literature cited at end of article.

## Experimental Procedure

The first prerequisite for the nylon staining technique is to have an exceptionally well prepared slide of yarn cross-sections, with the filaments free of damage from the cutting action. The paraffin embedding technique was used.[3]

Since nylon fibers are somewhat tougher than rayon, it was found that better sections were obtained by setting the rotary microtome to cut at 7$\mu$ thickness.

### *Preparation of the Stains*

An aqueous solution (1% by weight) of each of the dyes, Kiton Blue V and Methyl Violet, was prepared with distilled water. A volume of 200 cm.$^3$ was used in this case. The two dye baths were then placed on a thermostatically controlled hot plate and heated to 70° C. before insertion of the slide. The dye baths should be maintained at this temperature during the staining of nylon 6 yarn cross-sections. For the staining of nylon 66 yarn sections, it is necessary to raise the temperature of both dye baths to 90° C. before insertion of the slide.

[2] The Kiton Pure Blue V can be obtained from Ciba Co. Inc., Box 1988, Charlotte, N. C. The Methyl Violet 2B Supra I is supplied by Geigy Chemical Corp., Saw Mill River Road, Ardsley, N. Y.

[3] Tissuemat, supplied by Fisher Scientific Co. with a melting point of 56.5° C. was used.

*Staining Procedure*

1. The slide or slides (nylon 6) are first placed in the hot Kiton Blue V dye for approximately 3-min. staining time. The slide is then washed in distilled water to remove the excess dye. Microscopical examination of the filaments at this point reveals the skin to be stained a light bluish-green with the core portion a lighter shade of blue.

2. The slide is then placed in the Methyl Violet dye bath for approximately 25-sec. staining time, after which the excess dye is again removed by washing in distilled water. Examination of the filaments after the second bath reveals the skin portion of the filament to be stained a reddish-violet color with the core stained slightly violet.

3. The slide is then dried and mounted in Permount [4] for photomicrography. Sufficient contrast exists between the skin and core to make good photomicrographs without the use of any light filter. Figure 1 shows a photomicrograph of drawn, delustered nylon 6 filaments stained according to the procedure described above.

For staining undrawn nylon 6 cross-sections, less staining time is required in both dye baths than in the case of drawn nylon samples. In the first step (Kiton Blue V) approximately 45 sec. is sufficient, followed by a 10-sec. treatment in the Methyl Violet dye bath. Figure 2 is a photomicrograph of stained sections of delustered undrawn nylon 6 filaments.

To further substantiate that two types of structure (skin and core) exist in a nylon filament, and to further verify the validity of the staining technique, a sample of nylon 6 was stained so as to incorporate both dyes in the filament. In this case the core portion stained a reddish-purple, while the skin or outer membrane stained blue.

For staining nylon 66 cross-sections, as previously mentioned, the temperature of the dye baths must be raised to 90° C. before the insertion of the slides. The staining time must also be increased to 7 min. in the first step (Kiton Blue V) followed by a 50-sec. treatment with the Methyl Violet. All other conditions for staining nylon 66 are the same as

[4] The Permount is a 60% solution of synthetic resins obtained from Fisher Scientific Co.

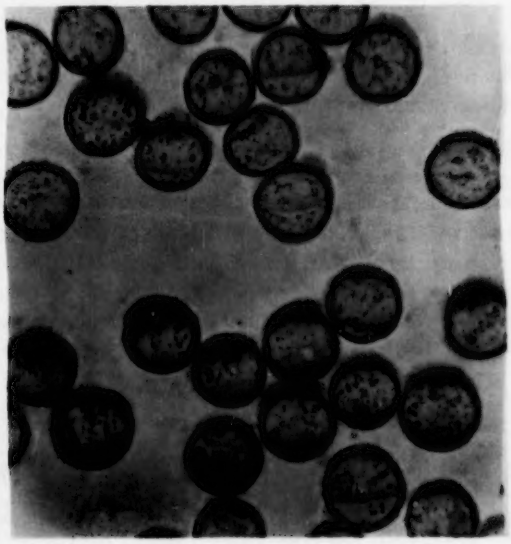


**Fig. 1.** Drawn delustered nylon 6 filaments.

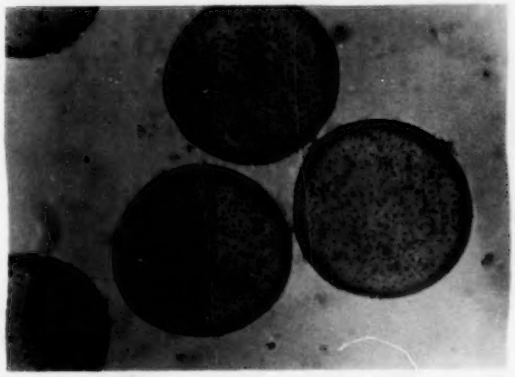


**Fig. 2.** Undrawn delustered nylon 6 filaments.

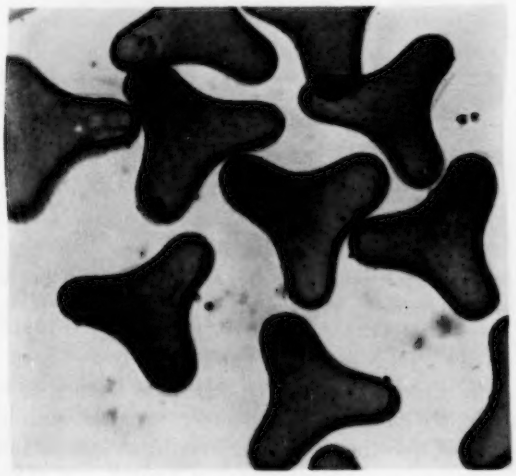


**Fig. 3.** Nylon 66 yarn.

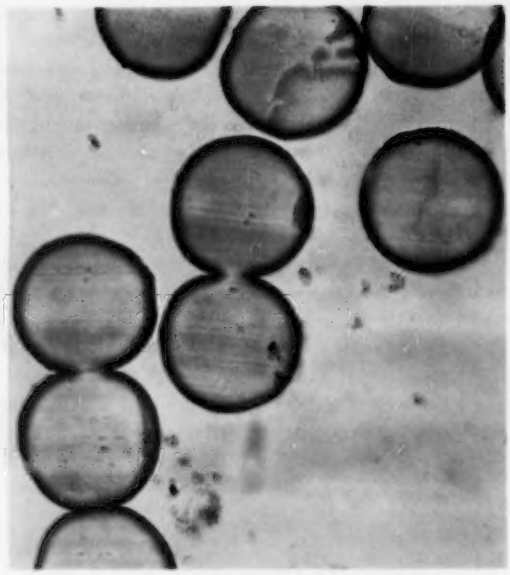


Fig. 4. Bright nylon 6, slow quench rate.

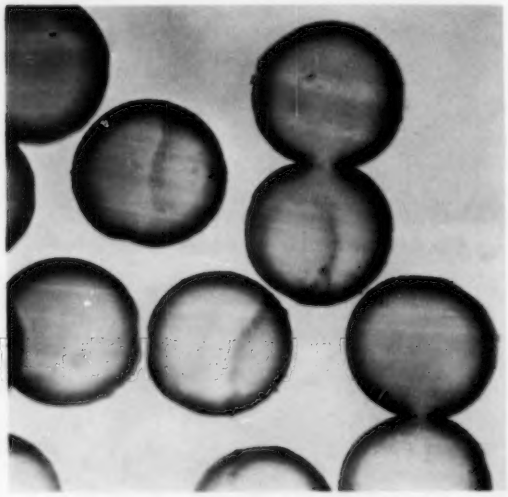


Fig. 5. Bright nylon 6, fast quench rate.

described for nylon 6. Figure 3 shows a nylon 66 sample stained as described.

## Discussion

Since the development of this nylon staining technique, the effects of melt spinning variables, such as rates of quenching, winding speeds, and variations in conditions of drawing on skin formation of nylon 6, have been studied. This type of investigation is still in progress, and although not conclusive, a number of interesting observations concerning the skin and core structure have been made, some of which will be mentioned here.

The quenching rate was found to be a factor influencing the amount of skin formed in spinning bright textile yarn. For example, with slow rates of quenching, it has been found that less skin area exists than at higher rates of quenching. Figures 4 and 5 show the stained undrawn filaments spun with different quenching rates. They indicate that the cooling rate of the molten filament has a definite influence on the formation of skin, as might be expected.

The investigation of skin areas of a number of undrawn and drawn yarn samples spun at various winding speeds indicated that, in general, the skin area increases as the winding speed increases. However, it should be mentioned that at some of the higher speeds the relationship of skin area and winding speed is not linear. In the case of each sample investigated, 7 to 10 filaments were measured and the areas averaged.

The variation in the extent of the skin area from filament to filament in the undrawn and drawn samples provides an interesting note. In the case of the undrawn samples, a spread of only 3% was found, while the drawn samples had skin variations of 6% to 7%.

Birefringence measurements were also made on the above series of samples with an average of the measurements of 10 filaments reported in each case. There appeared to be no direct correlation between skin area and birefringence.

## Summary

A new staining technique with water-soluble dyes has been developed for the differential staining of the skin and core of drawn and undrawn nylon 6 and 66 yarns. In initial investigations it has been found that variation in some of the conditions of melt spinning of nylon 6 affect the amount of skin area in both the drawn and undrawn yarn.

## Literature Cited

1. DeRiz, O., Hauptmann, B., and Schuller, E., *Melliand Textilber.* **35**, 680–685 (July 1955).
2. Schwertassek, K., *Faserforsch. u. Textiltech.* **6**, 45–53 (1955).
3. Schwertassek, K. and Plíšek, L., *Chem. Prûmysl* **8**(33), 216–218 (1958).

*Manuscript received January 26, 1961.*

# The Oxidation of Cotton Cellulose in the Presence of Direct Cotton Dyes

**K. V. Datye, G. M. Nabar, and G. G. Shroff**

*Department of Chemical Technology, University of Bombay, Bombay 19, India*

**Abstract**

Cotton cellulose dyed with direct cotton dyes was oxidized with buffered sodium hypochlorite solutions under different conditions. An attempt was made to correlate the extent of degradation of cellulose and the oxygen consumption during oxidation with the chemical constitution of dyes. The behavior of dyed samples during exposure to Fade-Ometer light has also been examined to study the influence of the constitution of the dyes. The results are discussed with a view to correlating the behavior of these dyes with that of leuco vat dyes under similar conditions.

## Introduction

The oxidation of cellulose is considerably enhanced when it is treated with a suitable oxidizing agent in the presence of easily oxidizable substances such as reduced vat dyes [3, 13, 20], certain metal hydroxides [19], basic chromium carbonate [2], etc. The enhanced oxidation of cellulose by sodium hypochlorite in the presence of leuco vat dyes and the properties of oxycellulose thus obtained have been investigated by various workers [11, 14, 17, 18, 23, 24]. It has been suggested that direct cotton dyes and vat dyes in solution are adsorbed by cellulose by more or less the same mechanism [26, 27]. One would, therefore, expect a similarity in the behavior of leuco vat dyes and direct cotton dyes when their cellulosic dyeings are treated with sodium hypochlorite under similar conditions. No attention has been paid so far to the influence of direct cotton dyes on the modification of the substrate during hypochlorite treatment of their dyeings. The present investigation is undertaken to study the oxidation of cotton cellulose dyed with direct cotton dyes and the properties of the resultant oxycelluloses, to see how far their behavior is similar to that of leuco vat dyes.

## Experimental

### *Materials*

*Cellulose.* Carefully purified and bleached 20's mixed yarn and plain cloth made from Indian cotton were used for the experiments. Cuprammonium fluidity [28] of their 0.5% solutions at 30° C. was between 4.0 and 5.0 poises$^{-1}$.

*Dyestuffs.* Commercial dyes were used. The dyes used for the study of the relationship between the chemical constitution and the tendering behavior of the dyeings were purified by the method of Robinson and Mills [21] and analyzed for their purity [12], which was found to be of the order of 98% ± 2%.

*Sodium hypochlorite.* A stock solution of sodium hypochlorite was prepared [15] and stored at about 5° C. in the dark. When required it was suitably diluted and buffered to give nearly 3 g. av. Cl/l. at the desired pH.

### *Methods*

*Dyeing.* Dyeing was carried out from a salt bath using 2% commercial or 1% pure dye on weight of the air-dried material as was required. The dye-liquor : material ratio was kept at 20 : 1 in the case of yarn and at 50 : 1 in the case of cloth. After dyeing, the yarn or cloth was washed with ice cold water, squeezed thoroughly between layers of filter paper, and dried at room temperature. An undyed sample was also treated similarly for control. The amount of dyestuff adsorbed by the fiber was estimated colorimetrically.

*Hypochlorite treatment of dyeings.* The dyed and undyed cotton yarns were treated with buffered solutions of sodium hypochlorite in the dark as well as in diffused daylight with a liquor : yarn ratio of 50 : 1 and stirred frequently to ensure uniform contact. At the end of the requisite time, the yarn was removed and washed with cold distilled water. Subsequently it was treated with a dilute solution of

sodium thiosulfate, washed free from soluble impurities with repeated changes of cold distilled water, and dried at room temperature. In some cases, the oxidation of the dye alone, equivalent in quantity to that present on the dyed fiber as found from colorimetric measurements, was carried out simultaneously under identical conditions. The oxygen consumption by the dyeing as well as by the dye alone was determined after correcting for hypochlorite self-decomposition.

*Exposure to light.* The dyed cloth was exposed for different periods to light using an Atlas Fade-Ometer. After exposure, the samples were rinsed with cold distilled water, dried at room temperature, conditioned, and analyzed for their cuprammonium fluidity [28]. The rise in cuprammonium fluidity of a sample as a result of both hypochlorite treatment and exposure to light is taken as a measure of the extent of chemical modification.

*Properties of the oxycellulose.* Reducing power (copper number) [10] and acidity (carboxyl content) [16] of the treated as well as exposed samples were determined both before and after chlorous acid treatment at 30° C. for 18 hr. [6].

## *Experimental Results*

The results are tabulated in Tables I–VII. The rise in cuprammonium fluidity of the dyeing due to hypochlorite treatment at pH 6.0 and 8.0 in the dark and that due to exposure to Fade-Ometer light for 75 hr. are reported in Table I. A few selected

**TABLE I. Increase in Cuprammonium Fluidity of Dyeings of Direct Cotton Dyes on Hypochlorite Oxidation and on Exposure to Fade-Ometer Light**

(More than 50 direct dyes belonging to different color groups were studied. Results for a few dyes are included in the Table.)

| Color index name of dye | Increase in cuprammonium fluidity: Hypochlorite oxidation in dark for 10 min. pH 6.2 | Hypochlorite oxidation in dark for 10 min. pH 8.0 | Exposure to Fade-Ometer light for 75 hr. |
|---|---|---|---|
| 1. Undyed (control) | 4.5 | 6.9 | 8.9 |
| 2. Direct Yellow 8 | 11.3 | 10.2 | 11.1 |
| 3. Direct Yellow 8 (aftertreated with copper sulfate) | 17.2 | 11.5 | 18.7 |
| 4. Direct Yellow 8 (aftertreated with chromium acetate) | 30.6 | 20.8 | 17.6 |
| 5. Direct Yellow 28 | 2.7 | 6.6 | 16.2 |
| 6. Direct Yellow 46 | 4.6 | 8.4 | 6.4 |
| 7. Direct Yellow 46 (aftertreated with chromium acetate) | 35.5 | 40.0 | 12.8 |
| 8. Direct Yellow 59 | 14.0 | 10.7 | 24.1 |
| 9. Undyed (control) | 4.5 | 6.9 | 6.2 |
| 10. Direct Orange 2 | 4.8 | 8.6 | 15.0 |
| 11. Direct Orange 15 | 5.5 | 6.2 | 15.0 |
| 12. Direct Red 1 | 18.7 | 11.6 | 5.8 |
| 13. Direct Red 2 | 24.8 | 21.3 | 7.1 |
| 14. Direct Red 17 | 20.7 | 16.5 | 11.6 |
| 15. Direct Red 28 | 22.9 | 18.1 | 8.0 |
| 16. Direct Red 82 | 24.2 | 19.1 | 5.0 |
| 17. Direct Violet 1 | 19.3 | 8.2 | 8.1 |
| 18. Direct Violet 12 | 10.1 | 10.8 | 6.7 |
| 19. Direct Violet 53 | 24.7 | 17.9 | 5.9 |
| 20. Direct Blue 1 | 6.5 | 7.7 | 16.7 |
| 21. Direct Blue 14 | 6.8 | 6.8 | 10.7 |
| 22. Direct Blue 71 | 15.4 | 13.4 | 6.3 |
| 23. Direct Green 6 | 14.0 | 12.9 | 9.3 |
| 24. Direct Brown 2 | 11.9 | 9.9 | 3.9 |
| 25. Direct Brown 2 (aftertreated with copper sulfate) | 30.6 | 20.8 | 9.4 |
| 26. Direct Black 67 | 14.1 | 10.3 | 9.1 |

**TABLE II. Effect of Light on Hypochlorite Oxidation of Dyeings of Direct Cotton Dyes**

| Color index name of dye | Increase in cuprammonium fluidity on hypochlorite oxidation for 10 min. at pH 6.2: In dark | pH 6.2: In diffused daylight | pH 8.0: In dark | pH 8.0: In diffused daylight |
|---|---|---|---|---|
| 1. Direct Yellow 12 | 8.7 | 11.4 | 4.0 | 8.9 |
| 2. Direct Yellow 28 | 2.7 | 5.2 | 6.6 | 7.6 |
| 3. Direct Orange 15 | 5.5 | 7.2 | 6.2 | 6.5 |
| 4. Direct Orange 48 | 7.5 | 9.8 | 11.2 | 14.8 |
| 5. Direct Red 1 | 18.7 | 24.0 | 11.6 | 14.1 |
| 6. Undyed (control) | 4.5 | 8.2 | 6.9 | 10.0 |
| 7. Direct Red 82 | 24.2 | 27.7 | 19.1 | 24.0 |
| 8. Direct Violet 1 | 19.3 | 23.9 | 8.2 | 13.2 |
| 9. Direct Blue 6 | 7.0 | 9.8 | 7.6 | 8.9 |
| 10. Direct Green 28 | 9.4 | 11.5 | 9.8 | 13.3 |
| 11. Direct Brown 95 | 5.1 | 9.7 | 6.0 | 10.4 |
| 12. Undyed (control) | 4.3 | 9.0 | 5.5 | 10.4 |

**TABLE III. Effect of Constitution of Dyes on Their Accelerating Activity in Hypochlorite Oxidation and on Exposure of their Dyeings to Fade-Ometer Light**

| Color index name of dye and C.I. constitution number | Middle component | End components | Increase in cuprammonium fluidity | | | | Oxygen consumption of the dyeing in hypochlorite oxidation for 10 min. in diffused daylight, milliatoms/100 g. dry cellulose | |
|---|---|---|---|---|---|---|---|---|
| | | | On hypochlorite oxidation in diffused daylight for 10 min. at | | On exposure to Fade-Ometer light for | | | |
| | | | pH 6.0 | pH 8.0 | 50 hr. | 100 hr. | pH 6.0 | pH 8.0 |
| Direct Red 28 (22120) | Benzidine | Naphthionic acid (2 mol.) | 25.8 | 17.3 | 2.6 | 16.4 | 18.4 | 12.9 |
| Direct Red 10 (22145) | Benzidine | Naphthionic acid and N.W. acid | 12.5 | 13.9 | 5.8 | 18.7 | 20.2 | 19.1 |
| Direct Violet 43 (22440) | Benzidine | N.W. acid (2 mol.) | 8.1 | 8.5 | — | — | — | — |
| Direct Red 2 (23500) | *o*-Tolidine | Naphthionic acid (2 mol.) | 20.3 | 14.7 | 5.1 | 17.6 | 16.8 | 14.6 |
| Direct Violet 21 (23520) | *o*-Tolidine | Naphthionic acid and N.W. acid | 10.6 | 8.9 | 5.4 | 9.4 | 10.1 | 13.1 |
| Direct Red 1 (22310) | Benzidine | Salicylic acid and γ acid (acid coupling) | 17.1 | 13.1 | 3.5 | 6.4 | 21.4 | 21.1 |
| Direct Brown 2 (22311) | Benzidine | Salicylic acid and γ acid (alkaline coupling) | 11.3 | 9.1 | 3.6 | 6.3 | 29.1 | 28.9 |
| Direct Red 33 (22306) | Benzidine | Salicylic acid and J acid (alkaline coupling) | 11.8 | 10.8 | 5.1 | 11.1 | 23.9 | 24.4 |
| Undyed (control) | — | — | 4.0 | 6.0 | 8.7 | 15.0 | 3.6 | 3.7 |

dyes were purified and their dyeings exposed to Fade-Ometer light for 50 and 100 hr. each as well as being treated with buffered dilute hypochlorite solutions in diffused daylight. [It was observed (Table II) that diffused daylight did not materially affect the course of oxidation.] The results of these investigations are given in Tables III and IV and are arranged according to the chemical constitution of the dyes. Dyes differing from each other with regard to substitution in the end components are included in Table III. The results obtained with dyes having different middle components are reported in Table IV. From the estimated amount of oxygen uptake by each of the dyeings, the calculated amount of oxygen consumed by an equivalent amount of dye alone is substracted so as to obtain the amount of oxygen consumed by the fiber, and these results are reported in Table V. The share of the dye and that of the substrate in the total oxygen consumption of a dyeing are evaluated on the assumption that the oxygen consumption by a dye while present on the substrate in the dyed form is the same as that in its absence. The increase in fluidity of some of the dyeings treated with hypochlorite solutions and that exposed to Fade-Ometer light are given in Table VI. Copper number and carboxyl content of some of the treated dyeings before and after chlorous acid treatment and the various relationships calculated from these are given in Table VII.

## Discussion

From the results in Table I, it is seen that the hypochlorite treatment of dyeings of direct cotton dyes for 10 min. in the dark results in an increase in the cuprammonium fluidity in all cases. The increase in cuprammonium fluidity of dyed samples is in most of the cases higher than that for the undyed sample. However, the extent of the increase in fluidity for the dyed samples varies from one dye to another. A high increase in fluidity is not confined to any particular color. Similarly all dyes of any particular color do not appear to bring about a high rise in fluidity. Aftertreated dyeings, however, exhibit a high rise in fluidity irrespective of the behavior of the corresponding untreated dyeings. This indicates that the presence of either copper or chro-

mium combined with the dye brings about an increased oxidation of the substrate. The fluidity of samples treated with sodium hypochlorite in the dark is always slightly lower than that of samples treated in diffused daylight (Table II). As the undyed yarn also exhibits higher fluidity when treated in diffused daylight than when treated in the dark, it is felt that the slightly higher fluidity of samples treated in diffused daylight rather than in the dark is of no particular significance and may be attributed to the activating influence of light on hypochlorite solutions. Oxygen consumption by dyeings during hypochlorite treatment in diffused daylight has no direct relationship with the increase in fluidity (Tables III–V). In order to illustrate the influence of pH of the oxidizing solution on the course of oxidation of direct dyeings, two dyeings and one undyed yarn sample were treated with buffered sodium hypochlorite solutions at different pH for 10 min. in the dark. The results are plotted in Figure 1. The maximum increase in fluidity results from treatment of the dyeings at pH 7. This is in conformity with the known behavior of hypochlorite solutions [7]. The results also help to illustrate the influence of the dye in enhancing the oxidation of the substrate over the pH range examined.

The variation in the increase in fluidity of dyeings of different dyes is due to the differences in the ability of dyes to receive oxygen from hypochlorite solution and to transmit it to the substrate. This may depend upon the chemical constitution of the dyes, their affinity, and their susceptibility to oxidation. The results indicate that dyes which are more resistant to hypochlorite oxidation bring about greater oxidation of the substrate than those which are easily oxidized (Table V). This is probably due to the fact that a dye which is oxidized easily may consume most of the oxidative energy for the process of self-modification or destruction and thus cannot transfer any appreciable amount to the substrate. However, a dye which is difficult to oxidize may consume relatively less energy and transfer the rest to the substrate. The influence of the affinity of the

**TABLE IV. Effect of Constitution of Dyes on Their Accelerating Activity in Hypochlorite Oxidation and on Exposure of their Dyeings to Fade-Ometer Light**

| Color index name of dye and C.I. constitution number | Middle component | End components | Increase in cuprammonium fluidity | | | | Oxygen consumption of the dyeing in hypochlorite oxidation for 10 min. in diffused daylight, milliatoms/100 g. dry cellulose | |
|---|---|---|---|---|---|---|---|---|
| | | | On hypochlorite oxidation in diffused daylight for 10 min. at | | On exposure to Fade-Ometer light for | | | |
| | | | pH 6.0 | pH 8.0 | 50 hr. | 100 hr. | pH 6.0 | pH 8.0 |
| Direct Red 28 (22120) | Benzidine | Naphthionic acid (2 mol.) | 25.8 | 17.3 | 2.6 | 16.4 | 18.4 | 12.9 |
| Direct Red 2 (23500) | *o*-Tolidine | Naphthionic acid (2 mol.) | 20.3 | 14.7 | 5.1 | 17.6 | 16.8 | 14.6 |
| Direct Red 7 (24100) | *o*-Dianisidine | Naphthionic acid (2 mol.) | 17.0 | 16.7 | 5.5 | 18.2 | 13.4 | 14.4 |
| Direct Red 61 (23040) | *o*-Dichlorobenzidine | Naphthionic acid (2 mol.) | 15.9 | 13.9 | 6.1 | 10.6 | 11.4 | 6.8 |
| Direct Red 10 (22145) | Benzidine | Naphthionic acid and N.W. acid | 12.5 | 13.9 | 5.8 | 18.7 | 20.2 | 19.1 |
| Direct Violet 21 (23520) | *o*-Tolidine | Naphthionic acid and N.W. acid | 10.6 | 8.9 | 5.4 | 9.4 | 10.1 | 13.1 |
| Direct Blue 6 (22610) | Benzidine | H acid (alkaline coupling) (2 mol.) | 8.0 | 6.6 | 8.5 | 12.9 | 15.9 | 14.4 |
| Direct Blue 14 (23850) | *o*-Tolidine | H acid (alkaline coupling) (2 mol.) | 7.6 | 5.6 | 8.2 | 15.8 | 15.7 | 14.2 |
| Undyed (control) | — | — | 4.4 | 5.1 | 8.7 | 15.2 | 3.8 | 4.6 |

**TABLE V. The Oxygen Consumption by the Dye, the Dyeing, and the Substrate in Hypochlorite Oxidation at pH 7 for 10 Min. in Diffused Daylight**

| Color index name of dye | Millimoles of dye/100 g. of dyeing | Milliatoms of oxygen consumed by: 100 g. dyeing (a) | The amount of dye in dyeing (b)* | 100 g. cellulose alone (a) − (b) | One millimole of the dye | Increase in cuprammonium fluidity |
|---|---|---|---|---|---|---|
| Direct Red 28 | 1.14 | 15.8 | 8.1 | 7.7 | 7.9 | 25.8 |
| Direct Red 2 | 1.14 | 12.6 | 7.4 | 5.2 | 6.5 | 23.4 |
| Direct Orange 8 | 1.15 | 19.2 | 13.4 | 5.8 | 11.7 | 18.3 |
| Direct Red 1 | 1.04 | 17.7 | 12.6 | 5.1 | 12.1 | 17.6 |
| Direct Red 17 | 0.63 | 11.3 | 5.7 | 5.6 | 8.9 | 14.4 |
| Direct Brown 2 | 0.95 | 23.6 | 18.9 | 4.7 | 19.9 | 11.5 |
| Undyed (control) | 0.00 | 3.8 | 0.0 | 3.8 | — | 9.4 |

* Calculated separately on the assumption that the oxygen consumption by a dye while present on the substrate in the dyed form is the same as that in its absence.

dyes can be seen from the results in Table VIII, in which the affinity values for a few dyes for cellulose and the rise in cuprammonium fluidity of their dyeings on hypochlorite treatment are given. The affinity values have been reproduced from published literature [25] and the corresponding fluidity values are taken from the present investigation. A closer examination of the results brings out very interesting relationships. It is seen that dyes having an amino group *ortho* to azo in both the end components absorb the least amount of oxygen from the hypochlorite solution and are less susceptible to oxidation; but dyes having an amino group in similar position in only one of the end components absorb more oxygen under similar conditions and are more susceptible to oxidation. Dyes having no such group in either of the two components exhibit maximum oxygen consumption and are the most susceptible to oxidation. The increase in cuprammonium fluidity follows, however, the opposite course. The increase in fluidity is maximum for dyeings prepared from dyes having an amino group *ortho* to azo in both end components. In the case of dyeings prepared from dyes having an amino group *ortho* to azo in only one of the two end components, the increase in fluidity is lower than that for the first group, but for dyeings of dyes having no such group in either of the end components, the increase in fluidity is the lowest. No significant change in the increase in fluidity of the dyeings takes place if the amino group in the end components is absent in the *ortho* position to the azo group (Table III). From the results in each group in Table IV, it may be noted that dyeings from dyes having benzidine as the middle component exhibit higher increase in fluidity and higher oxygen consumption during hypochlorite treatment than dyeings prepared from substituted benzidine dyes.

Atherton and Peters [1] have shown that the *ortho* amino azo dyes are difficult to oxidize due to steric hindrance, which protects the azo group. Desai and Giles [8] have also shown that the *ortho*-hydroxy-azobenzene is more easily oxidized

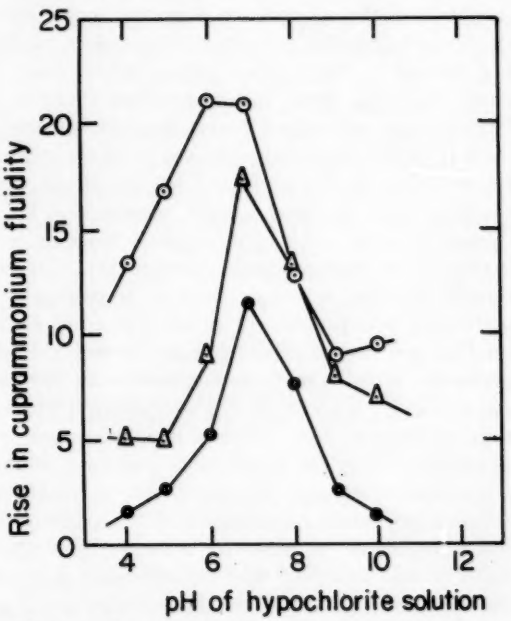



**Fig. 1.** Effect of pH of hypochlorite solution on the increase in cuprammonium fluidity of the dyeings. Time, 10 min. in the dark; temperature, 32° C.; material: liquor ratio, 1:50. ● = undyed control; ○ = C. I. Direct Red 1; △ = C. I. Direct Orange 48.

**TABLE VI. Comparison of the Activity of Dyes in Hypochlorite Oxidation of Their Dyeings and That on Exposure to Light**

| Color index name of dye | Increase in cuprammonium fluidity | |
|---|---|---|
| | On hypochlorite oxidation at pH 6.0 for 10 min. in diffused daylight | On exposure to Fade-Ometer for 50 hr. |
| Blank (undyed) | 4.4 | 8.7 |
| Direct Blue 14 | 7.6 | 8.2 |
| Direct Violet 3 | 9.5 | 7.2 |
| Direct Red 10 | 12.5 | 5.8 |
| Direct Red 7 | 17.0 | 5.5 |
| Direct Red 1 | 17.1 | 3.5 |
| Direct Orange 8 | 22.6 | 2.7 |
| Direct Red 28 | 25.8 | 2.6 |

than the corresponding other azobenzene derivatives. The results of the present investigation substantiate the above conclusions that the *ortho*-hydroxy-azo compounds are oxidized more easily than the corresponding *ortho*-amino-azo dyes. During their oxidation by hypochlorite solutions the *ortho*-amino-azo dyes (which are less easily oxidized) accelerate the oxidation of the substrate to a greater extent than do the corresponding *ortho*-hydroxy-azo dyes (which are themselves destroyed). Unlike the behavior of leuco vat dyes, these dyes themselves consume a large amount of oxygen during hypochlorite treatment of their dyeings in comparison to that consumed by the substrate (Table V). Therefore in the case of direct dyes the total oxygen consumption by a dyeing from hypochlorite solutions is more or less a function of their oxidative susceptibility. Hence, though the fiber substance receives proportionately more oxygen in presence of an active direct dye, the total oxygen consumption by such a dyeing (which is the sum of the oxygen consumption by the dye and the substrate) is less than that of a dyeing prepared from an inactive dye. Most of the direct dyes are destroyed during the hypochlorite treatment within a few minutes and may, therefore, cease to contribute towards the enhanced oxidation of the substrate if the treatment is continued for a longer time. Actually it was observed that the difference between the increase in fluidity of the dyeings of active dyes and that of the control sample was greater if the treatment was carried out for only 3 min. than when it was continued for 10 min. or even longer.

On examining the behavior of these dyes when their dyeings are exposed to Fade-Ometer light for 50 and 100 hr., it is found that most of the dyes are modified to an appreciable extent within the first 50 hr. of exposure. Dyed samples exposed for 50 hr. exhibit a lower increase in fluidity than does the exposed, undyed control. With increasing period of exposure, however, some of the dyed samples show a higher increase in fluidity than the undyed sample. Thus the direct dyes studied do not exhibit any phototendering activity during the first 50 hr. of exposure but, in some cases, exhibit accelerated tendering action during the period from 50 to 100 hr. This shows that the dyes are protecting the fiber substance from photodegradation during the initial stages of exposure, while the decomposition products of the dyes formed during the initial stages of exposure are probably catalyzing photochemical tendering of the substrate. It may be mentioned that Daruwalla and Peter [5] have observed similar behavior in the case of samples treated with optical brightening agents and exposed to Fade-Ometer light. They observed that even after the optical brightening agent had lost most of its fluorescence, the accelerated tendering action continued with increasing periods of exposure, which indicated that the decomposition products accelerated the phototendering of the substrate.

From the results of the treatment of dyed cotton with hypochlorite solutions and its photochemical modification, it appears that a few dyes are either active or inactive in both cases. It is also noticed that some of the dyes which appreciably enhance the hypochlorite oxidation, protect the fiber substance on exposure to light for a period of 50 hr. (Table VI). It has been suggested that fading of dyes is an oxidative process [9, 22] and dyes slowly fade due to small but continuous absorption of actinic energy. The absorbed energy, however, is not available to modify the substrate as most of it is used up by the dye in self destruction. Once the dye is oxidized and its decomposition products are formed on the substrate, they influence the course of the reaction, and either accelerate or retard the photodegradation of the substrate.

The results of the present investigation indicate that the behavior of direct cotton dyes during hypochlorite treatment of their dyeings in the dark is similar to that of leuco vat dyes under similar conditions [20]. It has been shown that certain vat dyes in the unreduced state accelerate the hypochlorite

**TABLE VII. Properties of Treated Dyeings, and Functions Thereof**

| Color index name of dye | Copper number: Increase in hypochlorite oxidation (a) | Copper number: After chlorous acid treatment (b) | Copper number: Decrease in chlorous acid treatment (a) − (b) | Carboxyl content, Millieq./100 g.: Increase in hypochlorite oxidation (c) | Carboxyl content, Millieq./100 g.: After chlorous acid treatment (d) | Carboxyl content, Millieq./100 g.: Increase by chlorous acid treatment (d) − (c) | Fall in copper number: Residual copper number on chlorous acid treatment (a) − (b) / (b) | Copper number: Carboxyl content before chlorous acid treatment (a) / (c) | Increase in carboxyl content: Decrease in copper number on chlorous acid treatment (d) − (c) / (a) − (b) |
|---|---|---|---|---|---|---|---|---|---|
| Direct Orange 8 | 0.76 | 0.42 | 0.34 | 1.43 | 1.94 | 0.51 | 0.80 | 0.53 | 1.50 |
| Direct Red 1 | 0.59 | 0.29 | 0.30 | 1.61 | 1.94 | 0.31 | 1.00 | 0.37 | 1.03 |
| Direct Red 2 | 1.01 | 0.46 | 0.55 | 1.52 | 2.13 | 0.61 | 1.20 | 0.66 | 1.11 |
| Direct Red 10 | 1.16 | 0.58 | 0.58 | 1.52 | 2.32 | 0.80 | 1.00 | 0.76 | 1.38 |
| Direct Red 17 | 0.70 | 0.34 | 0.36 | 1.47 | 1.84 | 0.37 | 1.00 | 0.48 | 1.03 |
| Direct Brown 2 | 0.52 | 0.26 | 0.26 | 1.20 | 1.46 | 0.26 | 1.00 | 0.43 | 1.00 |
| Free leuco* Indanthrene Brilliant Orange RK | These vat dyes are not affected when their dyeings are treated with dilute hypochlorite solutions | | | | | | 0.93 | 1.49 | 1.49 |
| Free leuco* Indanthrene Golden Yellow GK | | | | | | | 1.13 | 1.16 | 1.22 |
| Free leuco* Indanthrene Yellow 3R | | | | | | | 1.12 | 1.39 | 1.11 |
| Free leuco* Indanthrene Dark Blue BO | | | | | | | 1.42 | 1.48 | 1.28 |
| Free leuco* Indanthrene Blue RS | The color of these dyes is modified when their dyeings are treated with dilute hypochlorite solutions | | | | | | — | 0.72 | — |
| Free leuco* Ciba Blue 2B | | | | | | | — | 0.68 | — |
| Free leuco* Indanthrene Blue 5G | | | | | | | — | 0.59 | — |
| Free leuco* Caledon Jade Green XS | | | | | | | — | 0.60 | — |

* These results are reproduced from the work of Nabar and coworkers [14, 17, 24].

oxidation of cellulose only in the presence of light and are practically inactive in the dark [4, 7]. To explain this behavior, it is suggested that in the presence of light such vat dyes are reduced to their leuco form and in the presence of atmospheric oxygen are oxidized to the parent dye, resulting in a simultaneous oxidation of cellulose [23]. A leuco vat dye on hypochlorite treatment is oxidized to the parent vat dye but a direct cotton dye under similar circumstances is irreversibly destroyed. In the case of light exposure most of the vat dyes are not easily destroyed and hence the cycle of reduction–oxidation may take place a number of times. The substrate may thus be modified to a small degree in every cycle of reduction–oxidation, resulting in considerable cumulative degradative action. Since direct cotton dyes are modified irreversibly on exposure, the phenomenon which takes place in the case of vat dyeings does not occur in this case.

From the results of the chemical examination of the oxycelluloses formed by treatment of direct cotton dyeings with sodium hypochlorite solutions (Table VII), it is seen that the copper number and carboxyl content of the treated dyeings exhibit a simple relationship. The ratio between increase in copper number and increase in carboxyl content due to hypochlorite treatment is constant; also the ratio between decrease in copper number after chlorous acid treatment and residual copper number is nearly 1, and the ratio between increase in carboxyl content after chlorous acid treatment and decrease in copper number is also nearly 1. Similar simple relationships between these properties have been obtained by Nabar and coworkers [14, 17, 24] with oxycelluloses obtained from leuco vat dyeings treated similarly. A few of their results are included in Table VII to illustrate this point, and it will be observed that the various relationships between the properties of the

**TABLE VIII. Relation between the Affinity of Dyes and the Increase in Cuprammonium Fluidity of Their Dyeings on Hypochlorite Oxidation**

(Time = 10 min. in diffused daylight; pH of the hypochlorite solution = 6.0)

| Color index name of dye | Affinity of the dye for cellulose at 90° C., g.cal./mol. | Increase in cuprammonium fluidity |
|---|---|---|
| Direct Red 28 | −6920 | 25.8 |
| Direct Red 2 | −6700 | 20.7 |
| Direct Red 7 | −6550 | 17.0 |
| Direct Brown 2 | −6000 | 11.3 |
| Direct Blue 6 | −5120 | 8.0 |
| Direct Blue 10 | −4770 | 6.2 |

treated dyeings obtained from direct dyeings are similar to those for the treated leuco vat dyeings. From this similarity in the relationships between the properties of the treated dyeings of direct cotton dyes and those of leuco vat dyes, it is reasonable to conclude that the mechanism of oxidation of the substrate in the presence of these two classes of dyes is also similar.

## Summary

Direct cotton dyes enhance the hypochlorite oxidation of cellulose in the dark as well as in diffused daylight. Dyes having an amino group in the *ortho* position to the azo group in both the end components accelerate the hypochlorite oxidation of the substrate to a greater extent than do those having it in only one of the two end components; but dyes having no such group in either of the end components exhibit poor activity. Benzidine dyes enhance the hypochlorite oxidation of the substrate to a greater extent than *ortho* substituted benzidine dyes. Dyes which generally enhance the hypochlorite oxidation of the substrate to a greater extent are themselves susceptible to oxidation to a lesser extent than those which enhance it to a smaller extent. The color of the dyestuff, pH of the hypochlorite solution, and the presence of light during oxidation do not appear to influence the activity of these dyes. Direct cotton dyes appear to protect the substrate on exposure to Fade-Ometer light while their products of decomposition are found either to enhance or retard the phototendering of the substrate. Dyes which enhance the hypochlorite oxidation of the substrate to a maximum extent give good protection to the substrate during the first 50 hr. of exposure. The oxycelluloses obtained by hypochlorite oxidation of dyeings of direct cotton dyes exhibit simple relationships among their chemical properties.

## Literature Cited

1. Atherton, E. and Peters, R. H., *J. Soc. Dyers Colourists* **68**, 64 (1952).
2. Birtwell, C., Clibbens, D. A., and Ridge, B. P., *J. Textile Inst.* **16**, T13 (1925).
3. Brear, J. and Turner, H. A., *J. Soc. Dyers Colourists* **61**, 273 (1945).
4. Clibbens, D. A. and Little, A. H., *J. Textile Inst.* **37**, T219 (1946).
5. Daruwalla, E. H. and Peter, C. I., TEXTILE RESEARCH JOURNAL **31**, 263 (1961).
6. Davidson, G. F. and Nevell, T. P., *J. Textile Inst.* **39**, T111 (1948).
7. Derrett-Smith, D. A. and Nodder, C. R., *J. Textile Inst.* **23**, T293 (1932).
8. Desai, N. F. and Giles, C. H., *J. Soc. Dyers Colourists* **65**, 639 (1949).
9. Gebhard, K., *J. Soc. Dyers Colourists* **25**, 304 (1909); **26**, 173 (1910); **27**, 133 (1911); **34**, 74 (1918).
10. Heyes, T. F., *J. Soc. Chem. Ind.* **47**, T90 (1928).
11. Joshi, G. D. and Nabar, G. M., *Proc. Indian Acad. Sci.* **34**, 101 (1951).
12. Knecht, E. and Hibbert, Eva, "New Reduction Methods in Volumetric Analysis," 2nd edition, London, Longmans Green and Co., 1925, p. 97.
13. Mehta, D. N. and Turner, H. A., *J. Soc. Dyers Colourists* **63**, 15 (1947).
14. Mhatre, S. H., Nabar, G. M., and Vyas, G. M., *Proc. Indian Acad. Sci.* **31**, 234, 319 (1950).
15. Muspratt, M. and Smith, E. S., *J. Soc. Chem. Ind.* **17**, 1096 (1898).
16. Nabar, G. M. and Padmanabhan, C. V., *Proc. Indian Acad. Sci.* **31**, 371 (1950).
17. Nabar, G. M. and Padmanabhan, C. V., *Proc. Indian Acad. Sci.* **32**, 232 (1950).
18. Nabar, G. M. and Rathod, J. A., *J. Sci. Ind. Research (India)* **8B**, 81, 154 (1949).
19. Nabar, G. M. and Turner, H. A., *J. Soc. Dyers Colourists* **61**, 258 (1945).
20. Nabar, G. M., Scholefield, F., and Turner, H. A., *J. Soc. Dyers Colourists* **51**, 5 (1935); **53**, 5 (1937).
21. Robinson, C. and Mills, H. A. T., *Proc. Royal Soc.* **A131**, 579 (1931).
22. Scharwin, W. and Pakschwer, A., *Z. angew. Chem.* **40**, 1008 (1927); **41**, 1159 (1928).
23. Scholefield, F. and Turner, H. A., *J. Textile Inst.* **24**, P130 (1933).
24. Shenai, V. A., Ph.D. Thesis, University of Bombay, India (1960).
25. Urahata, T., *Kôgyô Kwagaku Zasshi* **59**, 1171–1176 (1956); **60**, 1468–1475 (1957).
26. Valko, E. I., TEXTILE RESEARCH JOURNAL **27**, 883 (1957).
27. Vickerstaff, T., "The Physical Chemistry of Dyeing," 2nd edition, London, Oliver and Boyd, 1954, p. 304.
28. "The Viscosity of Cellulose Solutions," London, Fabrics Research Committee, D.S.I.R., 1932; also *J. Textile Inst.* **27**, T285 (1936).

*Manuscript received January 26, 1961.*

# Radiation-Induced Interaction of Acrylonitrile with Cyanoethylated Cotton

**Robert J. Demint, Jett C. Arthur, Jr., and Wilbur F. McSherry**

*Southern Regional Research Laboratory,[1] New Orleans, Louisiana*

**Abstract**

The radiation-induced interaction of acrylonitrile with cyanoethylated cotton probably involves grafting of side chains of acrylonitrile at the site of the cyanoethyl groups. The extent of interaction is dependent on the degree of substitution of the cotton and on radiation dosage. There are increases in delayed elastic recovery and elongation-at-break and decreases in permanent set, average stiffness, and solubility of the cellulose of the treated cottons.

RADIATION-polymerization of acrylonitrile in the presence of cotton offered a new approach to the chemical modification of the physical properties of cotton [2–5, 9]. Cotton modified in this manner had polymer located within the fiber, increased elongation-at-break, decreased stiffness, and only a slight decrease in breaking strength [3]. The presence of chemical groups on modified cottons could offer sites for increased interaction of monomers with cellulose upon high-energy irradiation. This could result in further desirable changes in the physical properties of cotton. In this report, the radiation-induced interaction of acrylonitrile with cyanoethylated cotton and the properties of the modified cotton are discussed.

## Experimental

### *Materials*

Deltapine cotton, spun into 7s/3 yarn and wound into 18-yd. skeins, each weighing 4 g., was purified by extraction with hot ethanol followed by boiling in 1% NaOH solution, with proper precautions to prevent exposure to air [8].

A commercial grade of acrylonitrile (water saturated) and reagent grades of NaOH, $ZnCl_2$, and N,N-dimethylformamide were used.

### *Methods*

Cotton was cyanoethylated by padding onto the yarn a 2% NaOH solution to about 85% pickup and then immersing the yarn in acrylonitrile (water saturated), agitated at 55° C. The cotton was removed at predetermined times of reaction to give the desired degree of substitution, washed in dilute acetic acid, thoroughly rinsed in distilled water, and dried under ambient conditions [7].

Radiation-induced interactions of acrylonitrile with both purified and cyanoethylated cottons were carried out as follows. The yarn was immersed overnight at room temperature in a solution containing 32 parts of acrylonitrile monomer in 68 parts of aqueous 80% $ZnCl_2$ and then padded to give about a two- to fourfold increase in weight of the original yarn. The treated cotton was irradiated in the SRRL cobalt-60 source [1], which had a dose rate of about $0.5 \times 10^6$ roentgens/hr. (maximum). Under optimum conditions, about 70–80% of the monomer interacted with the cotton. Unreacted monomer was removed by washing the irradiated cottons with distilled water; loosely interacted monomer was removed by extraction of the cottons overnight at room temperature with N,N-dimethylformamide in the ratio of about 4 g. of yarn to 75 ml. of solvent, followed by washing with water and drying overnight at room temperature. The content of nitrogen was determined using the Kjeldahl method [6]. The content of cyanoethyl groups and interacted monomer was calculated from the unextractable nitrogen content. It was also determined that irradiation of cyanoethylated cotton did not decrease its degree of substitution, that is, its nitrogen content.

The solubility of the cellulose in the products was measured by dispersing 0.5 g. of the product in 100 ml. of 0.5 *M* cupriethylene diamine. Then the weight of the insoluble fraction of the product and its nitro-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

gen content were determined. From these data the solubility of the cellulose was calculated.

A gauge length of 10 in. and a rate of specimen extension of 50%/min. were used with the Instron [2] for stress–strain determinations. Elastic recovery properties were determined using the modified single-specimen technique, described by Susich and Backer [10], and a rate of extension of 20%/min.

## Results

### *Degree of Substitution*

The effect of degree of substitution (DS) on the radiation-induced interaction of acrylonitrile with cyanoethylated cotton and on its properties is shown in Table I. With an increase in DS from about 0 to 1.3, the amount of monomer interacted with the yarn increased about fourfold; elongation-at-break and yarn number increased; average stiffness decreased markedly; and breaking strength and toughness decreased slightly. At 1.3 DS, the composition of the fibrous product was about 36% cellulose, 15% cyanoethyl groups, and 49% interacted monomer. Fibrous products from cyanoethylated cottons having DS's greater than about 0.7 exhibited some shrinkage during treatment.

### *Radiation Dosage*

The effect of radiation dosage on the interaction of acrylonitrile with cyanoethylated cotton, DS 0.7, and on its properties is shown in Table II. The maximum interaction of acrylonitrile with the cyanoethylated cotton was at dosages from about 0.8 to 1.5 megaroentgens. With increasing interaction of acrylonitrile, elongation-at-break and yarn number increased, average stiffness decreased, and breaking strength and toughness increased slightly. At 0.8 megaroentgen, the composition of the fibrous product was about 51% cellulose, 11% cyanoethyl groups, and 38% interacted monomer.

### *Elastic Recovery Properties*

The effect of radiation-induced interaction of acrylonitrile with cyanoethylated cotton, DS 0.7, on its elastic recovery properties is shown in Table III. The fibrous product had an interacted monomer content of about 38%, or 74 parts of interacted monomer to 100 parts of cellulose. At elongations of the fibrous product of 25% or less of its elongation-at-break, decreases in permanent set and increases in delayed recovery of the yarns were observed. There was apparently no effect on the immediate recovery of the yarns. These changes indicate that a stabilizing of molecular bonds occurred (increased delayed recovery and decreased permanent set) but that the bonds involved were apparently low in energy (little or no change in immediate recovery).

### *Solubility of the Products*

The solubility of the cellulose of the cotton products in 0.5 *M* cupriethylene diamine is shown in Table IV. The solubilities of purified and cyano-

[2] Trade names are given as part of the exact experimental conditions and not as an endorsement of the products over those of other manufacturers.

**TABLE I. Effect of Degree of Substitution on the Radiation-Induced Interaction of Acrylonitrile with Cyanoethylated Cotton and on Its Properties ***

| Property of yarn† | Degree of substitution | | | | | | |
|---|---|---|---|---|---|---|---|
| | 0.00‡ | 0.00 | 0.34 | 0.57 | 0.72 | 0.99 | 1.29 |
| Interacted monomer content, % | 0 | 26 | 33 | 32 | 35 | 38 | 49 |
| Parts monomer to 100 parts cellulose | 0 | 35 | 55 | 56 | 66 | 81 | 136 |
| Breaking strength, lb. | 10.1 | 8.8 | 7.6 | 7.5 | 8.4 | 8.9 | 8.5 |
| Elongation-at-break, % | 13 | 23 | 28 | 29 | 29 | 29 | 33 |
| Yarn number, tex | 241 | 401 | 557 | 590 | 628 | 747 | 1054 |
| Breaking toughness, g./tex | 0.79 | 0.73 | 0.60 | 0.62 | 0.70 | 0.70 | 0.59 |
| Average stiffness, g./tex | 141 | 43 | 22 | 19 | 21 | 18 | 11 |

* Treating solution: 32 parts of acrylonitrile in 68 parts of aqueous 80% $ZnCl_2$. Radiation dosage, 1.0 megaroentgen.
† Instron properties.
‡ Purified, untreated, unirradiated yarn.

**TABLE II. Effect of Radiation Dosage on the Interaction of Acrylonitrile with Cyanoethylated Cotton and on Its Properties ***

| Property of yarn† | Dosage, megaroentgen | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 0.0‡ | 0.0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 | 1.5 |
| Interacted monomer content, % | 0 | 0 | 1 | 4 | 27 | 38 | 38 | 36 |
| Parts monomer to 100 parts cellulose | 0 | 0 | 1 | 5 | 45 | 74 | 74 | 69 |
| Breaking strength, lb. | 10.1 | 6.2 | 7.1 | 6.7 | 6.3 | 7.4 | 8.2 | 7.0 |
| Elongation-at-break, % | 13 | 12 | 15 | 17 | 24 | 26 | 28 | 24 |
| Yarn number, tex | 241 | 298 | 312 | 345 | 513 | 656 | 649 | 622 |
| Breaking toughness, g./tex | 0.79 | 0.40 | 0.61 | 0.53 | 0.48 | 0.55 | 0.64 | 0.49 |
| Average stiffness, g./tex | 141 | 76 | 67 | 53 | 24 | 20 | 21 | 21 |

* Treating solution: 32 parts of acrylonitrile in 68 parts of aqueous 80% $ZnCl_2$. Degree of substitution of cotton, 0.7.
† Instron properties.
‡ Purified, untreated, unirradiated yarn.

ethylated cottons, products A and C, were almost 100%. The solubility of the cellulose in product B, which contained radiation-polymerized acrylonitrile, was about 50%. From the magnitude of the increase in the nitrogen content of the insoluble fraction of product B over that of total product B it could be calculated that only cellulose dissolved. The solubility of the cellulose in product D, which contained cyanoethylated cotton and radiation-induced interacted monomer, was about zero. The relatively constant nitrogen content indicated little or no change in the product.

### *Mechanism of the Interaction of Monomer with Cotton*

The relationships between the interaction of monomer with cyanoethylated cotton and degree of substitution at a dosage of one megaroentgen are shown in Figure 1. Interacted monomer per 100 units of cellulose increased linearly over a range from 0.0 to about 1.0 DS and then increased rapidly.

The weight ratio of change in interacted monomer to change in cyanoethyl group, as compared with the data for purified cotton containing polymer both calculated to 100 units of cellulose, was about 1.5. The interacted monomer is composed of the same type of groups as the cyanoethyl groups; this would indicate that on the average about 1.5 additional groups for each cyanoethyl group were added by the high-energy-radiation-induced interaction.

The weight ratio of cyanoethyl groups to interacted monomer increased to about 0.34 at about 0.6 DS and then remained relatively constant over the range investigated. This would indicate that on the average about 3 additional groups were added for each cyanoethyl group by the radiation-induced interaction. In the estimation of the value of 1.5 added groups for each cyanoethyl group, it was assumed

**TABLE III. Effect of Radiation-Induced Interaction of Acrylonitrile with Cyanoethylated Cotton on its Elastic Recovery Properties ***

| Elongation of cotton,† % of elongation-at-break | Recovery,† % of actual elongation | | |
|---|---|---|---|
| | Purified | Purified cyanoethylated | Cyanoethylated irradiated |
| | *Immediate recovery* | | |
| 5 | 30 | 34 | 34 |
| 10 | 23 | 29 | 24 |
| 25 | 9 | 10 | 9 |
| 50 | 6 | 8 | 5 |
| 75 | 6 | 7 | 4 |
| | *Delayed recovery* | | |
| 5 | 49 | 49 | 63 |
| 10 | 58 | 55 | 71 |
| 25 | 66 | 69 | 74 |
| 50 | 46 | 46 | 48 |
| 75 | 29 | 30 | 29 |
| | *Permanent set* | | |
| 5 | 21 | 17 | 3 |
| 10 | 19 | 16 | 5 |
| 25 | 25 | 21 | 17 |
| 50 | 48 | 46 | 47 |
| 75 | 65 | 63 | 67 |

* Degree of substitution, 0.7. Radiation dosage, 1 megaroentgen. See Table II for other properties of the cottons.
† Instron properties.

**TABLE IV. Solubility of Cellulose in the Product ***

| Cotton product† | Solubility of cellulose, % | Nitrogen, % | |
|---|---|---|---|
| | | Total | Insoluble fraction |
| A | 99 | — | — |
| B | 48 | 6.6 | 10.2 |
| C | 97 | 4.8 | — |
| D | 0 | 13.0 | 11.5 |

* Solvent: 0.5 *M* cupriethylene diamine.

† A: purified cotton. B: purified cotton, irradiated 0.8 megaroentgen, containing 25% polymer. C: cyanoethylated cotton, DS 0.67. D: cyanoethylated cotton (DS 0.67), irradiated 0.8 megaroentgen, containing 38% interacted monomer.

that the interaction of monomer with the purified cotton occurred in the same manner and to the same extent as with the cyanoethylated cotton. Consequently, the amount of monomer interacted with cotton was subtracted from the amount interacted with the cyanoethylated cotton before calculating the additional groups.

However, if it were assumed that monomer interacted with the substituted cotton at the site of the cyanoethyl groups, the value of about 3 groups added by radiation-induced interaction per cyanoethyl group would probably be more reasonable. This type of interaction was indicated by the direct relationship between DS and interaction of acrylonitrile, by the low solubilities of the cellulose and the interacted acrylonitrile in the product, and by the relative constancy of the immediate elastic recovery of the yarns. The latter property indicated the absence of cross-links or possibly the presence of cross-links having very weak bonds. It was concluded that the principal mechanism of radiation-induced interaction of acrylonitrile with cyanoethylated cotton was probably a grafting reaction.

## Summary

The radiation-induced interaction of acrylonitrile with cyanoethylated cotton probably involved grafting of side chains of acrylonitrile at the site of the cyanoethyl groups. The extent of interaction was dependent on the degree of substitution of the cotton and on radiation dosage. There were increases in delayed elastic recovery and elongation-at-break and decreases in permanent set, average stiffness, and solubility of the cellulose of the treated cottons.

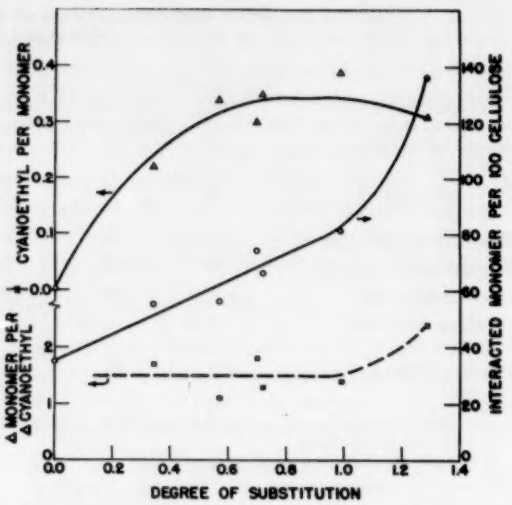



**Fig. 1.** Relationships between interaction of monomer with cyanoethylated cotton and degree of substitution. Dosage: 1 megaroentgen.

## Acknowledgment

The technical assistance of J. F. Jurgens in performing some of the tests reported is gratefully acknowledged.

## Literature Cited

1. Arthur, J. C., Jr., Blouin, F. A., and Demint, R. J., "The SRRL Cobalt-60 Facility," U. S. Dept. Agr., *ARS 72-21*, 7 pp. (August 1960).
2. Arthur, J. C., Jr. and Demint, R. J., *J. Phys. Chem.* **64**, 1332 (1960).
3. Arthur, J. C., Jr. and Demint, R. J., TEXTILE RESEARCH JOURNAL **30**, 505–509 (1960).
4. Arthur, J. C., Jr., Demint, R. J., McSherry, W. F., and Jurgens, J. F., TEXTILE RESEARCH JOURNAL **29**, 759 (1959).
5. Arthur, J. C., Jr., Demint, R. J., and Pittman, R. A., *J. Phys. Chem.* **63**, 1366–1368 (1959).
6. Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 8th ed., Washington, D. C., 11–12 (1955).
7. Daul, G. C., Reinhardt, R. M., and Reid, J. D., TEXTILE RESEARCH JOURNAL **25**, 246–253 (1955).
8. Kettering, J. H. and Conrad, C. M., *Ind. Eng. Chem., Anal. Ed.* **14**, 432–434 (1942).
9. Rutherford, H. A., Armstrong, A. A., Jr., Kiser, L. H., and Kirby, R. D., TEXTILE RESEARCH JOURNAL **30**, 546 (1960).
10. Susich, G. and Backer, S., TEXTILE RESEARCH JOURNAL **21**, 482–509 (1951).

*Manuscript received February 27, 1961.*

# Letters to the Editor

## The Influence of Surfactants in the Acid Bath on the Loss in Strength of Carbonized Wool[1]

Harris Research Laboratories, Inc.
6220 Kansas Avenue, N.E.
Washington 11, D. C.
April 17, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

Several years ago, Crewther [2] described a new method for protecting wool from the loss of tensile strength, during carbonizing, by the addition of wetting agents to the acid bath. Anionic, cationic, and nonionic agents were all effective and provided adequate protection over a wide range of concentrations. More recently, Crewther and Pressley [3] found that nonionic agents containing an alkyl or aryl hydrocarbon group were particularly effective, whereas other nonionic agents, in which the lipophilic portion consists of polyoxypropylene, provided little protection. They also indicated that no direct evidence concerning the mechanism of the protective action of surface active agents in carbonizing had yet been obtained but that the structure of the wetting agent may be an important factor. This subject was very recently discussed by other Australian workers [1].

Industrial processors have tried this method with inconclusive results. Personal communications from several wool carbonizers in this country indicated that in actual practice either a protective action from the use of wetting agents had not been realized, or, on occasion, an improvement in wool strength was observed when wetting agents were used. Both discussions and written communications with Dr. Crewther also pointed out that in his experience the effect was not always obtained under Australian mill conditions. Recently French workers [4] have indicated the importance of the moisture content of wool prior to baking in carbonizing.

In a study undertaken for the Western Utilization Research and Development Division of the U. S. Department of Agriculture, we have investigated many factors involved in carbonizing, and especially the effects of wetting agents in the acid bath. The results of our complete study will be published at a later date. However, data have been obtained which we believe provide a rational explanation of the "protective" effect produced by the presence of wetting agents, and which also explain why this "protective" effect is not always obtained. These data, and a mechanism which accounts for the puzzling results obtained by other workers in research and industry, are submitted in this letter.

A commercially scoured raw wool, containing spiral burrs, was treated with acid so as to contain 6.5% ± 0.2% of sulfuric acid after extraction, based on the conditioned (65% RH at 70° F.) weight of the acid-containing wool. Other samples were similarly treated with acid containing 0.05% of various wetting agents. The acid-treated and extracted burry wool samples were air dried at 100° F., with the aid of a fan, to various wool moisture contents, based on the weight of the wool, just prior to baking. Each sample was baked for 3 min. at 300° F., neutralized, conditioned, and tested for breaking strength.

The results, in a plot of breaking strength as a function of moisture content of acid-containing wool as it enters the baking oven, are given in Figure 1. It is evident from these results that the presence of wetting agents per se in the acid bath *do not* protect wool from loss in tensile strength during carbonizing. The important factor is the moisture content of the acid-containing wool as it enters the dryer or oven. We find that certain types of surfactants in the acid bath cause more liquor, i.e., acid *and water,* to be expressed from the wool by either squeeze roll or centrifugal extractions than is extracted from the same wool sample when no surfactant is present. It is this *lower water content* of the extracted wools,

[1] A report of work done under contract with the U. S. Department of Agriculture and authorized by the Research and Marketing Act of 1946. The contract is being supervised by the Western Utilization and Development Division of the Agricultural Research Service.

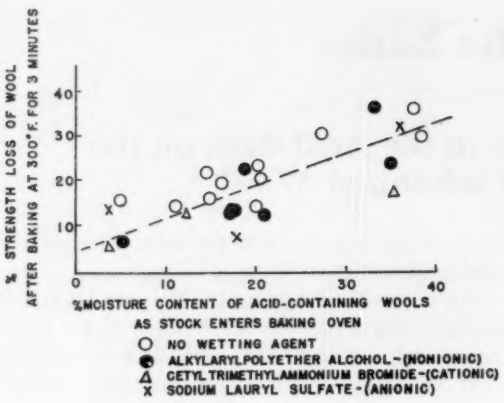



Fig. 1.

treated in acid-surfactant baths, which causes them to lose less tensile strength than is lost by the acid-treated wool extracted to a higher moisture content. Slightly stronger acid solutions were used when the wetting agent was present so that the same amount of acid was on the wool in both cases after extraction. Thus, in keeping with the moisture–strength relationship found above, for identical conditions of extraction, a sample prepared with surfactant in some cases will contain less moisture and, consequently, will show a lower loss of strength on baking than one prepared in the absence of wetting agent. An extraction method, such as high speed centrifuging, may reduce the moisture content of the wool to such a value that "protection" is apparently afforded by the wetting agent. For example, an extraction method which results in a moisture content of 15%, and a strength loss of 17% (after baking with 6.5% acid on wool) in the absence of a surfactant, may result in a moisture content below 10% and a negligible strength loss when a surfactant is used. The factor governing the strength loss is the moisture content of the wool and not the presence of the surfactant. In fact, we were able to obtain damage, or avoid it, with the identical wetting agent in the bath by adjusting the moisture content of the extracted wool, proving that moisture was the governing factor. This is the explanation for conflicting results by various workers unaware of this factor.

We should point out that the addition of a small amount of a wetting agent, 0.01% to 0.02%, to the acid bath also greatly aids in wetting the extracted wool and burrs (previously wetted from preceding scouring and rinse bowls) with acid, and this contributes to complete charring of the burrs during the baking operation. Further, the treatment of raw wool with sulfuric acid plus wetting agent generally gives a cleaner, whiter, fluffier stock in addition to better carbonization of the vegetable matter than is obtained from the same wool treated in acid without wetting agent. Therefore, the Australian discovery of the beneficial effects of surfactants in the carbonizing process, aside from considerations of effects on the breaking strength of the fibers, is a most important one.

In addition to the above factor, the two other important factors which influence loss in strength during carbonizing are the actual air temperature used to dry the wet, extracted, acid-containing wool, and the acid content of the wool as it enters the dryer. All three factors are interrelated in their effects on the strength of the wool, and by proper adjustment of conditions, the vegetable matter can be completely charred without any measurable loss in strength of the wool. A full report on these conditions will be submitted soon.

In summary, we find that wetting agents per se do not protect the wool during carbonizing, but they have an indirect beneficial effect on the tensile strength of the wool by reducing the water content of the extracted, acid-treated material just prior to drying or baking. We hope that these findings will clarify the controversy about the influence of wetting agents in the acid bath on the tensile strength of the wool during carbonizing.

## Literature Cited

1. Buchsbaum, N. and Datyner, A., *J. Soc. Dyers Colourists* **77**, 16 (1961).
2. Crewther, W. G., *Proc. Int. Wool Textile Res. Conf., Aust.* **E**, 408, 596 (1956).
3. Crewther, W. G. and Pressley, T. A., TEXTILE RESEARCH JOURNAL **29**, 483 (1959).
4. Wilbaux, G., Mazingue, G., and Van Oberbeke, M., *Bull. inst. textile France*, No. 83, 85–97 (1959).

A. ELEANOR DAVIS
ANNA J. JOHNSON
LOUIS R. MIZELL

# Heat Shrinkage Tensions of Nylon Tire Cord

British Nylon Spinners Limited
Pontypool, Monmouthshire
England
May 3, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

In an article [1] in this JOURNAL, Wood, Goy, and Daruwalla described a constant length tensometer for measuring thermal shrinkage forces and gave some results. This note draws attention to the time dependence of the results which this type of experiment gives. Their Figure 21 showed maxima in the tension–temperature curves for various materials. They took readings with the instrument in the oven, as the temperature rose, over a period of about 30 min. [2]. We have found, using a similar apparatus, that the position of these maxima for nylon 6.6, nylon 6, and polyester are time dependent. The maximum occurs at higher temperatures if the time at which the tension is observed is decreased to a few seconds, the time which it takes to put the instrument in the oven and for it to respond. In our experiments the tensometer was placed in an already hot oven. The tension was noted after 15 sec. and after 5 min.; the maximum tension developed was also recorded. Figure 1 shows results obtained on nylon 6.6, 2/840 B.N.S. Type 600 cord, 12S/12Z twist. Nylon 6 and polyester exhibit similar behavior. The curve we obtained for readings taken 5 min. after the tensometer was immersed in the oven is similar to that shown by Wood et al. [1]. At a time as long as 5 min., appreciable stress decay occurs at temperatures above 220° C. Similarly above 240° C., appreciable stress decay takes place in 15 sec. At still higher temperatures some decay presumably occurs before the instrument responds fully. Up to 200° C., the maximum tension recorded and the 5-min. reading were the same; at 220° C., the maximum tension and the 15-sec. reading were identical. At 240° C. and above, the tension maximum occurred before 15 sec. and is recorded separately on Figure 1. These results suggest that the cord tension necessary to hold to length increases up to the melting point. Tensions were recorded up to 280° C., that is, above the melting point of nylon 6.6.

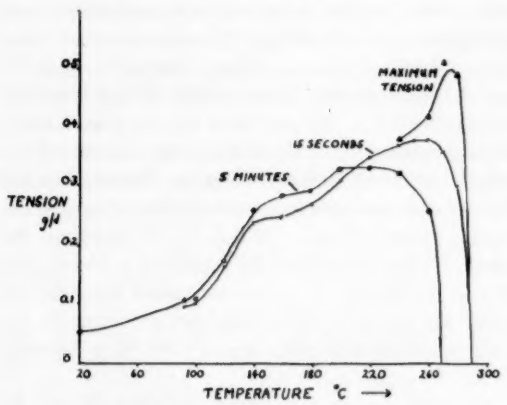


Fig. 1.

It may be possible to use the tension developed by a cord to estimate the effectiveness of the heat transfer medium in which it is placed. This would involve using a tension measuring device with a rapid response compared with the cord heating time. Then the rate at which the tension built up would be an indication of the rate at which the cord was heating.

## Literature Cited

1. Wood, J. O., Goy, R. S., and Daruwalla, F. S., TEXTILE RESEARCH JOURNAL **29**, 669–678 (1959).
2. Wood, J. O., private communication.

W. S. SYMES

# Twisted Bundle Ballistic Tests of Jute Fiber under Longitudinal Jerk

Technological Research Laboratories
Indian Central Jute Committee
Calcutta-40, India
May 23, 1961

To the Editor
TEXTILE RESEARCH JOURNAL

*Dear Sir:*

The ballistic tester is a common instrument. It measures the total energy [5] consumed in breaking a fiber bundle, yarn, or piece of cloth to rupture by a sudden blow, irrespective of the fact that the individual elements do not sustain the same amount of elongation at break. One such instrument was designed in this laboratory for breaking jute fiber bundles [6], and the values for the ballistic work of rupture were found to be significantly correlated with yarn breaking length. Later, testing of twisted bundles was preferred because twisting partially imitates the condition of fibers in yarn. The packing effect of twist brings the fibers into closer contact, prevents slippage, and at the same time reduces the effective free (ungripped) length of the filaments. These factors invariably increase bundle strength; the oblique disposition of the fibers, on the other hand, reduces bundle strength approximately by a factor, $\cos^2\theta$, where $\theta$ is the angle at which the surface fibers lie with respect to the bundle axis, or simply the twist angle [4].

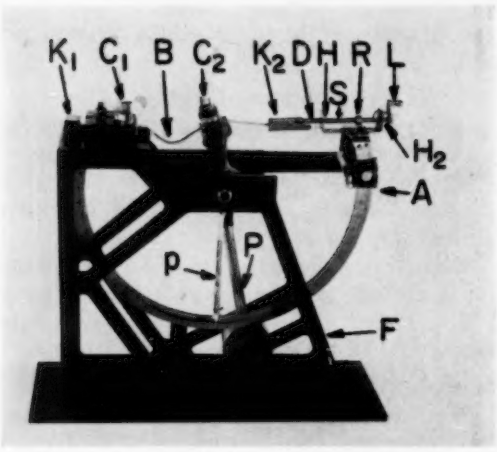


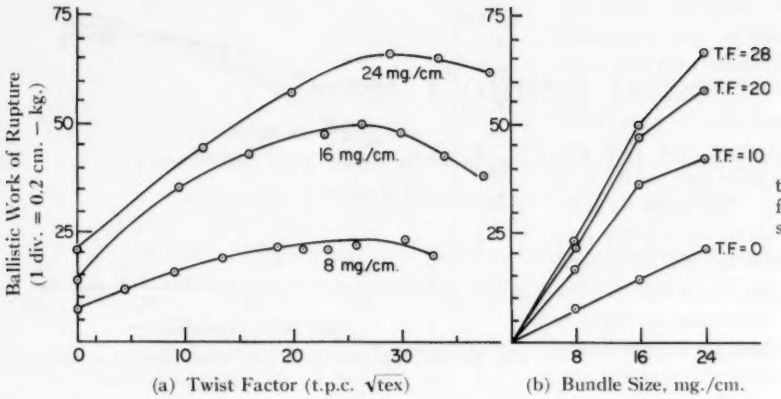

**Fig. 1.** The ballistic tester with twisting device.

For ballistic tests of twisted jute fiber bundles, a fiber mounting device was introduced [2] in a Goodbrand yarn ballistic tester; but the blow could only be applied transversely. The results were, therefore, somewhat dependent on the shape and size of the striker and also on the angle formed at the striker by the two segments of the bundle just before breaking. This angle on the other hand is dependent on the tension on the bundle after clamping and on fiber extensibility, both of which are often variable. In spite of all these possible errors the ballistic work of rupture of 80-mg./cm. bundles, tied at both ends, under optimum twist condition was significantly correlated [1, 2] with yarn breaking length both for *olitorius* and *capsularis* jute.

## Experimental

The present instrument was designed to insert twist on the bundles to be broken by logitudinal jerk. In Figure 1, the pendulum, P, mounted on ball bearings, pointer, p, the corrugated clamps, $C_1$ and $C_2$, and the metal frame, F, constitute the old fiber ballistic tester [6]. To put twist on the fiber bundle, B, before clamping at $C_1$ and $C_2$, the two ends of the bundle are held without tying at clamps, $K_1$ and $K_2$, by the saw-toothed, spring-pressed grips extending over 1.5 cm. While $K_1$ is fixed on the frame, $K_2$ can be rotated by means of a 10-cm. rod, D, and the handle, L. The rod passes through two holes, $H_1$ and $H_2$, of a 7-cm. bridge fixed on the frame on adjustable slots, and a ring, R, is screwed on it.

A helical spring, S, inserted between $H_1$ and R allows for the take-up due to twist and keeps the bundle under tension, which may increase to about 300 g.-wt., corresponding to a contraction of 2 cm. After putting the requisite amount of twist on the bundle it is fixed on the clamps, $C_1$ and $C_2$, 10 cm. apart. As the pendulum is now raised to its starting position, A, the bundle end at $K_2$ is drawn off the grip and the clamp, $K_2$, automatically recedes back to its normal position by the action of the released spring, S. To prevent jaw breakages at high twists,




(a) Twist Factor (t.p.c. $\sqrt{\text{tex}}$) (b) Bundle Size, mg./cm.

**Fig. 2.** Ballistic work of rupture of twisted jute fiber bundles as functions of twist factor and bundle size.

the depth of the clamp corrugations at $C_1$ and $C_2$ are kept below 1 mm., and some leather padding is used.

Jute bundles of sizes up to 25 mg./cm. can be safely gripped at $K_1$ and $K_2$ even when twisted hard. One advantage of such spring grips is that as twist increases fibers on the outer layer pull off gradually from the grips so as to allow for a greater length required by them for spiralling round the bundle. This largely prevents bulking or kink formation in the central layers and excessive strain on the outer layers, as observed when the bundle ends are tied up.

Using a heavier bob, the capacity of the instrument at full scale (100 divisions) is about 20 kg.-cm. units of energy.

With this instrument the effect of twist on the ballistic work of rupture under longitudinal jerk was investigated in the case of a good quality *capsularis* jute. After proper sampling and light combing treatment, several representative fiber bundles of sizes 8 mg./cm., 16 mg./cm., and 24 mg./cm. were made up. A bundle length of 28 cm. was found convenient for a test length of 25 cm. between $K_1$ and $K_2$. The take-up due to twist as noted on a fine scale was as high as 7% for the heaviest bundle at the optimum twist point. The bundle diameter was also measured simply by means of a screw gauge without applying pressure. Twenty bundles were tested for each twist.

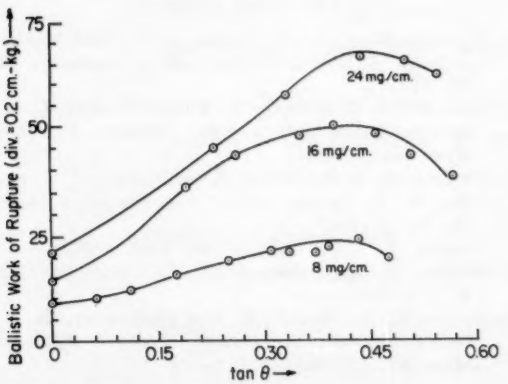



**Fig. 3.** Ballistic work of rupture of twisted jute fiber bundles of different sizes as function of twist angle.

## Results and Discussions

It is well known that the strength of a fiber bundle is dependent on the twist angle, $\theta$, and the relation is given by

$$\tan\theta = T\pi d \tag{1}$$

where $T$ = the number of turns/cm., and $d$ = the bundle diameter in cm. When $d$ is expressed in terms of tex-count and the packing density, $D$, of the bundle in g./cm.$^3$, we have

$$\tan\theta = T\sqrt{\frac{4\pi}{10^5}}\sqrt{\frac{\text{tex}}{D}} = \frac{F}{\sqrt{D}}\sqrt{\frac{4\pi}{10^5}} \tag{2}$$

where $F$ represents the product $T\sqrt{\text{tex}}$, known as twist factor.

The values of the ballistic work of rupture (b.w.r.) as obtained at different twists are plotted, in Figure 2a, against the twist factor, $F$, after correcting both $T$ and tex for length contraction. In Figure 3, the work of rupture is also plotted against $\tan\theta$, calculated directly from the corrected value of $T$ and $d$. This gave an estimate of the effect of changes in

packing density, which was obtained from the weight of the bundle, its diameter and contracted length. The nature of its variation with the twist factor, $F$, is shown in Figure 4.

The maximum value of b.w.r. lies between twist factors 27 and 29 in tex t.p.c. units (or 11.7 and 12.6 in grist t.p.i. units) or between tan$\theta$ values 0.42 and 0.45 for each bundle size. This value is only slightly above the optimum twist factor [3] for jute yarn, which usually lies between 23 and 25 in tex t.p.c. units (10 and 11 in grist t.p.i. units). At intermediate twists, however, the curves in Figures 2a and 3 apparently differ in shape, the former showing convexity and the latter concavity towards the b.w.r. axis. This difference may be explained on the basis of the packing density, which gradually increases from a low value at low twist factor to a fairly constant value of about 0.55 g./cm.$^3$ near the optimum twist factor, as shown in Figure 4. This range of variation of $D$ would, however, be smaller had measurement of $D$ been made at breaking tension. The change in the nature of curvature is obviously the result of diminution of the density of packing at lower twist factors, which comparatively shortens the intervals of the abscissa in that region of Figure 3.

The proportionality of the b.w.r. values to the initial size of the bundle has been checked by plotting, in Figure 2b, the b.w.r. values against bundle size at different twist factors. While the line at zero twist is clearly straight, that at optimum twist deviates slightly from linearity, and at intermediate twists the deviations are quite appreciable. This also is possibly due to the fact that though at optimum twist factor the packing density of the bundles is fairly consistent for all the sizes, at intermediate twists the density varies to some extent because the packing conditions are somewhat variable at the low twisting tensions provided in this instrument.

On the question of the accuracy of estimation, at optimum twist factor the standard error is lowest, being about 4% of the mean, against 5% at other conditions. But at zero twist there is the possibility of using thicker bundles to reduce the error. The cause of higher standard error for untwisted bundles has been traced to the difficulty of clamping some of the peripheral fibers at the sides. This has been overcome in a later modification in which at both clamps, $C_1$ and $C_2$, rectangular grooves 1.5 mm. wide and 12 mm. deep have been cut; the bundle is pressed into these by a close-fitting steel plunger, using thin leather padding above and below the bundle.

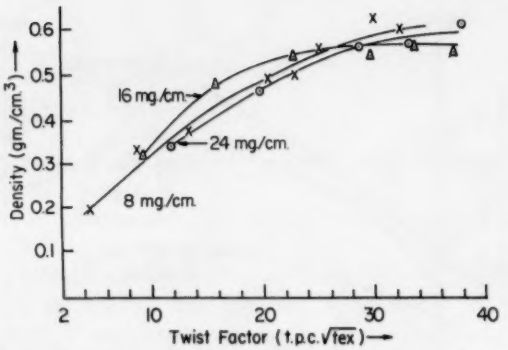



**Fig. 4.** Packing density of jute fiber bundles at different twist factors for different bundle sizes.

## Conclusion

For investigations on the quality of bast fibers of different types, one should confine the twisted-bundle b.w.r. tests to the optimum twist factor region, keeping in mind that even then the results may not be strictly proportional to bundle size. Fiber fineness and other properties which affect packing density may alter the optimum point as well. The b.w.r. tests of heavier, untwisted bundles clamped in rectangular grooves, on the other hand, would give a simpler index, which can be easily corrected for bundle-weight variation, if necessary; such an index would be suitable for comparing the energy characteristics of all types of bast fibers irrespective of fineness, surface structure, stiffness, etc.

## Literature Cited

1. Bandyopadhyay, S. B., Chatterjee, U., and Mukhopadhyay, S. K., *Fibres (Natural & Synthetic)* **15**, 295 (1954).
2. Chakrabarti, B. K., Sen, K. R., and Nodder, C. R., *Indian Central Jute Comm., Technol. Research, Mem.* No. 5 (1944).
3. Chakrabarti, B. K., Gillies, A. S., Nodder, C. R., and Sen, K. R., *Indian Central Jute Comm., Technol. Cir.* No. 2 (1945).
4. Gregory, J., *J. Textile Inst.* **44**, T505 (1953).
5. Midgley, E. and Peirce, F. T., *J. Textile Inst.* **17**, T317 (1926).
6. Nodder, C. R., Sen, K. R., and Chakrabarti, B. K., *Indian Central Jute Comm., Technol. Research Mem.* No. 2 (1940).

S. B. BANDYOPADHYAY
B. K. BOSE

# In Coming Issues

Quantitative Investigation of the X-Ray Diffraction Picture of Some Typical Rayon Specimens, Part II. *P. H. Hermans and A. Weidinger*

Studies of High Fastness to Light in Coloring Matters in Hydrophilic Substrates. *C. H. Giles, George Baxter, and S. M. K. Rahman*

The Statistical Interpretation of Fiber Counts in Yarn Cross-Sections. *D. N. E. Cooper*

Some Aspects of Capillary Absorption in Fibrous Textile Wicking. *R. D. Laughlin and J. E. Davies*

The Effect of the Short Fibers in a Cotton on its Processing Efficiency and Product Quality. Part III: Pilot-Scale Processing of Yarns. *J. D. Tallant, L. A. Fiori, D. M. Alberson, and W. E. Chapman*

A Statistical Procedure for Determining End Breakage in Spinning. *E. F. Schultz, H. M. Little, J. D. Tallant, and L. A. Fiori*

Cross-Linking Etherified Cottons with Dimethylol Ethyleneurea. *R. M. Kullman, J. G. Frick, Jr., R. M. Reinhardt, and J. D. Reid*

Physical Properties of Wool Fibers at Various Regains. Part III: Study of the State of Water in Wool by N. M. R. Techniques. *G. W. West, A. R. Haly, and M. Feughelman*

The Relationship of Fine Structure to Mechanical Properties of Stretched Saponified Acetate Fibers. *B. S. Sprague and H. D. Noether*

The Use of Coreactant Curing Agents with a Diepoxide to Impart Wrinkle Resistance to Cotton Fabrics. *R. M. Reinhardt, R. M. Kullman, H. B. Moore, and J. D. Reid*

Adsorption of Calcium and Polyphosphates on Cotton Cellulose and its Effect on Soil Deposition. *B. J. Rutkowski and A. R. Martin*

A Quantitative Study of Cotton Differential Dyeing as a Means of Elucidating Fiber Structure. *L. Rebenfeld and H. Wu*

# WASH & WEAR

**Crease Resistance**

by

acidifying Glyoxal solutions with

GLYOXYLIC ACID 40% Solution

acting as catalyst, with combined acid-aldehyde function.

The acid condensates with the fiber by formation of acetal at $pH_2$ to $pH_4$.

## GLYOXYLIC ACID

Now available in tonnage quantities

DR. F. JONAS COMPANY

55 West 42nd Street New York 36, N. Y.